2000

The Dehydrochlorination Mechanism of the Internal Allylic Chloride Structure in Poly(Vinyl Chloride)

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THE DEHYDROCHLORINATION MECHANISM OF THE INTERNAL ALLYLIC CHLORIDE STRUCTURE IN POLY(VINYL CHLORIDE)

A Thesis

Presented to

The Faculty of the Department of Chemistry

The College of William and Mary in Virginia

In Partial Fulfillment

Of the Requirements for the Degree of

Master of Arts

by

Lynda B. Payne

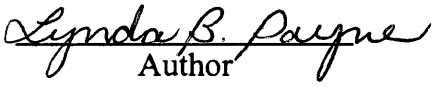
August, 2000

APPROVAL SHEET

This thesis is submitted in partial fulfillment of

the requirements for the degree of

Master of Arts



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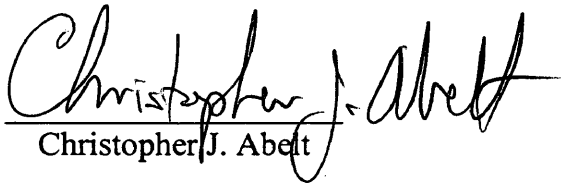

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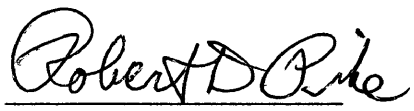

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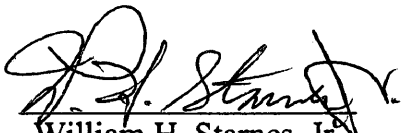

William H. Starnes, Jr.

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ACKNOWLEDGMENTS

The writer wishes to express her appreciation to Professor William H. Starnes, Jr., whose support and guidance for the duration of this project have been extremely helpful. She also wishes to thank Vadim Zaikov, Xianlong Ge, Ying Li, and Bin Du for their assistance in the laboratory. Finally, she is indebted to the Department of Chemistry at the College of William and Mary for the experiences and opportunities that she has gained as a result of her education.

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ABSTRACT

Poly(vinyl chloride) (PVC) is a thermally unstable material that rapidly loses hydrogen chloride upon heating to temperatures at or above 150 °C. The loss of HCl may occur at a number of possible structural defects within the polymer. The mechanism for the thermal dehydrochlorination at a chloroallylic defect is thought by many workers to be a 1,2 elimination involving an ion pair or a highly polarized four-center transition state. Another proposed mechanism for the dehydrochlorination involves the rearrangement at the chloroallylic structure into a *cis*-allylic configuration that subsequently loses HCl through a six-center concerted process. In the research described here, 2-chloro-1-ethylidenecyclohexane (actually, a mixture of isomers) was prepared by a three-step route and subjected to thermal dehydrochlorination at 170 °C. The rate of this reaction was found to be in line with expectations for *sec*-allylic chloride moieties such as those in PVC, and the dehydrochlorintion was found to form *cis*- and *trans*-3-ethylidenecyclohexene, rather than 1-vinylcyclohexene. These results are shown to argue strongly against a concerted six-center process for the thermal loss of HCl.

THE DEHYDROCHLORINATION MECHANISM FOR THE INTERNAL ALLYLIC CHLORIDE STRUCTURE IN POLY(VINYL CHLORIDE)

I. INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the oldest and most important commercially produced plastics in the world. With production beginning in the 1930's in the United States, the average annual use of PVC has greatly increased, and we are now likely to encounter PVC in several aspects of our lives every day. It has been estimated that the annual world consumption of PVC in 1996 totaled 23 million tons.[1] The usefulness of the polymer is still being expanded, and its production is likely to continue rising in the future.

For several years, PVC has been subjected to extensive research. Many issues are being investigated, such as the degradation processes of the polymer, its thermally labile sites, environmental issues, etc. The main intent of this thesis is to assess some continuing discrepancies in the literature regarding the thermal dehydrochlorination mechanism of an allylic chloride structural defect in PVC. First, an overview of the structural characteristics of the polymer and some of the research speculations will be explored, in order to give the reader insight into two different mechanisms that have been proposed for the thermal dehydrochlorination of an internal allylic chloride group.

Synthesis of PVC

Poly(vinyl chloride) is made up of repeating monomer units of vinyl chloride. Subjecting vinyl chloride to a free-radical source leads to the formation of the polymer (Figure 1).

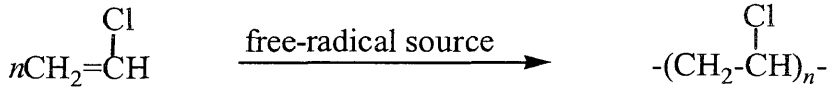


Figure 1. Synthesis of PVC.

Several different processes, such as emulsion, suspension, and mass polymerization are used for the manufacture of this material.[2] Formation by suspension polymerization is currently the most common method, producing up to 75% of the world's supply of PVC.[3]

Polymerization follows a generalized mechanism involving initiation, propagation, and termination. During initiation, radicals are produced in pairs from the decomposition of an initiator (I) (eq 1).

$$I \longrightarrow 2I\bullet \qquad (1)$$

The initiator radicals subsequently add to the monomer (M), vinyl chloride (eq 2).

$$I\bullet + M \longrightarrow P\bullet \qquad (2)$$

Propagation involves the continual addition of monomer molecules to P• radicals, resulting in chain growth (eq 3).

$$P\bullet + M \longrightarrow P_{n+1}\bullet \qquad (3)$$

The addition of monomer usually occurs in a head-to-tail manner in order to maintain the thermodynamic stability of the growing free radical. However, occasional head-to-head addition of monomer is possible. Addition in that manner results in the formation of a high-energy structure which rearranges by a 1,2 chlorine atom shift and then undergoes the abstraction of a chlorine atom by vinyl chloride.[4] The latter reaction results in chain transfer to the monomer, a process that is very important for controlling the molecular weight of the polymer during polymerization. In order to increase the molecular weight, the monomer concentration should be kept high.

Propagation will continue until two radicals interact with each other and terminate polymerization by coupling or disproportionation. Coupling reactions occur when two radicals combine to form a bond between the two radical-containing atoms (eq 4). Termination via coupling leads to a large increase in the molecular weight of the polymer.

$$P_n^{\bullet} + P_m^{\bullet} \longrightarrow P_{n+m} \qquad (4)$$

Disproportionation occurs when an atom (usually hydrogen) is abstracted from one radical species by another radical (eq 5). A saturated group is formed at the end of

one polymer chain, and a double bond is formed between the two carbons at the end of the other polymer molecule.

$$P_n^{\bullet} + P_m^{\bullet} \longrightarrow P_n(+H) + P_m(-H) \qquad (5)$$

Properties of PVC

Poly(vinyl chloride) has several advantageous properties. It is regarded as one of the most durable plastics produced. This polymer is insoluble in most solvents and resistant to corrosion and weathering, properties that allow it to be excellent for use in building construction materials.[1]

A feature that is of great importance and is very admirable to consumers is the long "lifespan" of these polymers. Unless they are used at high temperatures, these materials remain stable for extended lengths of time. In addition to having good stability, they are inexpensive to manufacture, and the polymer, itself, requires little maintenance, making it cost-effective. The extent to which PVC has been thermally degraded can be tested by using an instrumented drop weight impact test on PVC samples that have been aged at temperatures above their glass-transition temperature.[5] This test is useful for estimating the length of time the polymer retains its useful properties and for determining the overall extent of degradation after long-term aging.

Materials in landfills are commonly burned for disposal. Burning materials containing PVC has caused growing concern environmentally because of the corrosive and toxic hydrogen chloride gas that is given off. However, this polymer is essentially

resistant to fire when it does not contain plasticizers. Because of this property, PVC can be used as a protective covering for materials that burn easily.[1]

When PVC is heated in air to temperatures where it does burn, benzene is formed from the polyene sequences and burns with a smoky flame. The conjugated polyene structure can be modified (usually by crosslinking) in order to prevent benzene formation. Polyene formation is discussed briefly in the following section of this chapter.

One disadvantage among the properties of this polymer is its thermal instability. There are several speculations on the cause of this instability, and several attempts, many of them successful, have been made to solve this problem.

Additives

During the production and end use of most polymers, additives are necessary for stabilization, lubrication, plasticization, etc., in order for the polymers to retain their desirable characteristics. The use of stabilizers in the processing of PVC can slow the production of hydrogen chloride from the thermal degradation. Plasticizers, in addition to giving the polymer its flexibility, prevent embrittlement and cracking of the polymer. Plasticizers will soften the polymer to aid in the formation of a pliable material during the manufacture of PVC.

The weatherability of PVC is an important consideration to manufacturers because of the common use of this polymer as a construction material. The presence of oxygen results in the formation of hydroperoxide groups that affect the stability of the polymer and its duration of use. Most polymers will degrade in the outdoor environment

at rates that are dependent on their chemical structure. Within several weeks, the polymers tend to become brittle without the addition of stabilizers or antioxidants after the polymerization.[6] Ultraviolet (UV) absorbers are additives that are frequently used to prevent color formation resulting, in part, from the photodegradation of PVC. In the UV absorption spectrum of PVC, a band appears at 250 nm.[7] Pure PVC does not have structures that are expected to absorb at this wavelength. The most obvious structures in PVC giving rise to this band are polyene sequences. These sequences are now considered to be the main photoinitiators in PVC absorbing at 250 nm.[7] Ultraviolet absorbers can be added to polymers such as PVC and are capable of absorbing photons and then dissipating their energy by radiationless decay to the polymer matrix.[7] Additionally, additives that react with the polyene chromophores can prevent or reduce the color formation in the polymer by shortening polyene length.[8]

Thermal Degradation of PVC

Unstabilized PVC undergoes nonoxidative thermal degradation when it is heated to temperatures at or above 100 °C. The initiators of this degradation and thus the main contributors to the thermal instability are thought to be primarily the structural defects within the PVC. The formation of these defects may occur during the polymerization process and/or during heating of the polymer.

Regardless of the site of initiation, once dehydrochlorination begins, the loss of one molecule of hydrogen chloride generates an allylic chloride structure, which is a thermally unstable site within the polymer. The hydrogen chloride has an

autocatalytic effect on degradation that results in the sequential elimination of HCl without the loss of monomer and thus leads to the formation of polyene sequences.

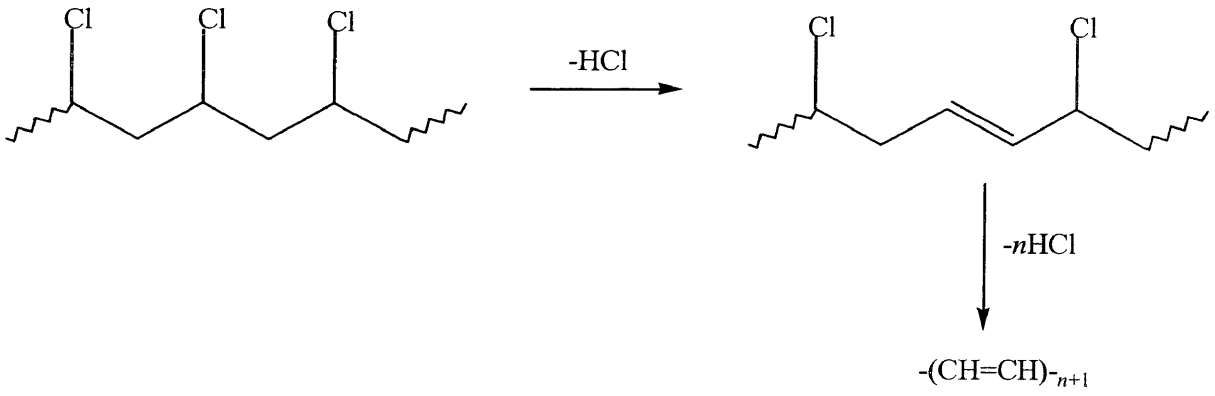


Figure 2. Formation of an internal allylic chloride structure and a polyene sequence in PVC.

Polyene sequence formation is favorable because of the additional resonance stabilization that this process involves. The longer the polyene sequences, the faster the rate of dehydrochlorination. The tacticity of the polymer is also a factor in determining the amount of HCl that is generated during the degradation. The isotactic configuration liberates HCl with the most facility.[9,10]

The polymer is initially colorless. However, polyene growth adds color to it at less than 0.1-0.2 weight % of HCl loss.[7] The color transition proceeds from colorless to yellow to black, depending on the number of double bonds present.

The dehydrochlorination will terminate along the polyene sequence once it contains anywhere from 5 to 25 conjugated double bonds.[8] A structural defect within the polymer may be encountered that leads to termination, or the dehydrochlorination may undergo an interruption reaction where the process is randomly stopped.[8]

Possible Structural Defects

There are differences in opinion as to the cause of the initiation of the thermal dehydrochlorination. The relatively unstable structural irregularities in the polymer are known to be very low in abundance. These irregularities contain easily removable tertiary or allylic chlorine atoms.[9]

The microstructure of PVC resin and the polymerization mechanism have been investigated by ^{13}C NMR, but have given researchers little additional information regarding the process of degradation. If the ^{13}C spectrum of the polymer itself were examined, many peaks due to structural defects would be hidden by the complex resonances of the ordinary monomer units, which occur in different tactic sequences. As discussed by Starnes,[11] in order to solve this problem, tri-*n*-butyltin hydride can be used in the presence of a free-radical source in order to replace all of the chlorines with hydrogens. The ^{13}C spectrum of the resultant polymeric product can then be used to determine the carbon skeleton. To determine the placement of the chlorines in the original polymer, tri-*n*-butyltin deuteride is used in the same way to replace the chlorines with deuteriums. The resonances of the deuterated carbons and the carbons to which those carbons are attached will be shifted upfield.[10]

As indicated above, most researchers agree that the main initiators of dehydrochlorination are structural defects containing labile chlorines. These structures are formed during the polymerization process in different manners. Keeping the monomer concentration high will decrease their abundance.[4] Figure 3 illustrates the formation of a dichlorobutyl branch.[9]

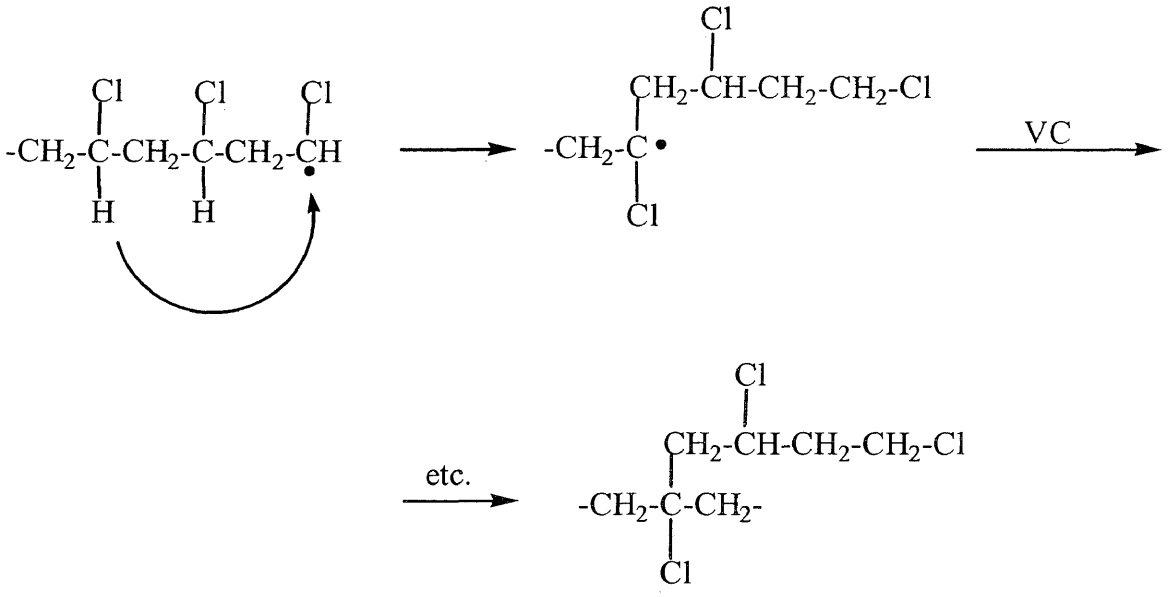


Figure 3. Dichlorobutyl-branch structure formation.

In the formation of this branch structure, an intramolecular "backbiting" reaction takes place within the propagating radical. Vinyl chloride adds to the new radical to produce a tertiary chloride, which is thermally unstable. The formation rate of the dichlorobutyl branch is not affected as the concentration of monomer decreases. However, this decrease will reduce the rate of normal propagation and thereby increase the number of dichlorobutyl branches in the polymer per unit mass.[12]

Another labile structure leading to the initiation of dehydrochlorination is the long-branch structure. The formation of this defect is shown in Figure 4.[9] The propagating polymeric radical, P•, abstracts a chloromethylene hydrogen from a polymer molecule to form a new radical that will add monomer.

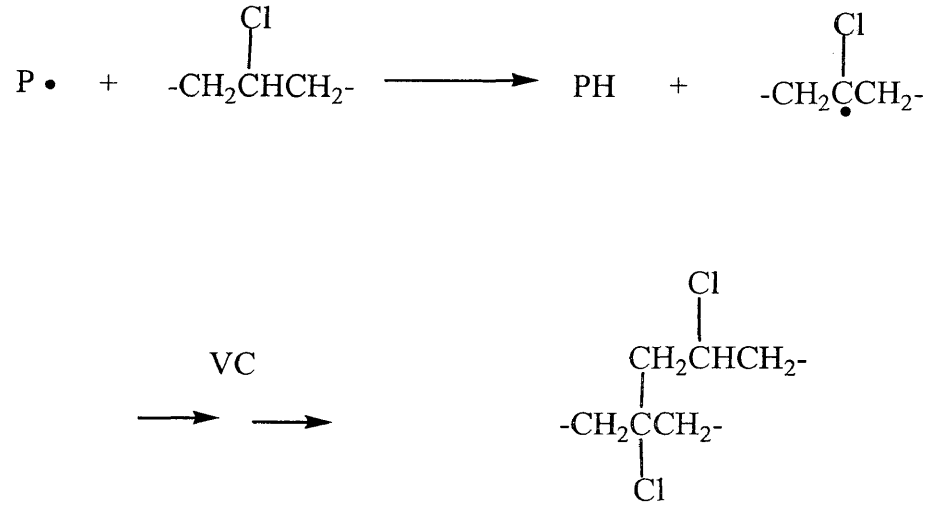


Figure 4. Long-branch structure formation.

For the purpose of studying the degradation mechanism of PVC, resins have been prepared that contain larger than normal concentrations of tertiary and allylic chlorines. When compared to the degradation rate of normally synthesized PVC, the rates for these resins were found to be significantly greater during the initial stages of degradation. Once the structural defects were exhausted, the rates slowed to that of normal PVC.[8]

Other possible structures leading to the initiation of degradation are the ketochloroallylic structure, -CO-CH=CH-CHCl-, and the internal chloroallylic (IA) structure.[7,9] The formation of the ketonic structure would be most likely to occur by air oxidation of the latter one, as shown in Figure 5. However, conclusive evidence for the presence of the ketonic structure is lacking.[10]

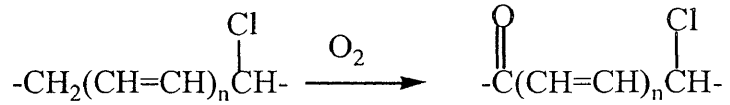


Figure 5. Formation of the ketochloroallylic structure in PVC.

In addition to the process shown in Figure 2, formation of the IA structure is known to occur during polymerization by the mechanism in Figure 6.[9,10]

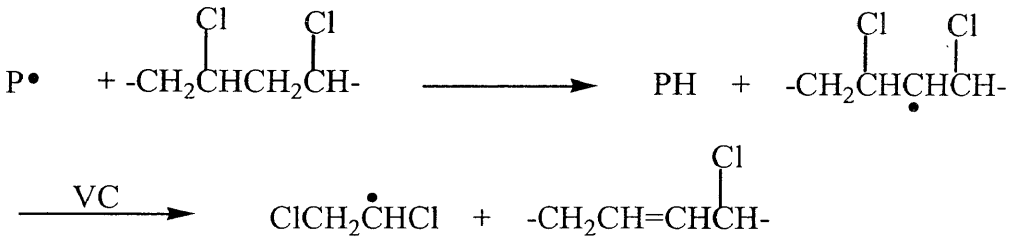


Figure 6. Alternative mechanism for the formation of the internal chloroallylic structure.

Several other structural defects are known to be present within the polymer, but they are not expected to increase the instability.[9] The head-to-head addition of monomer to an ordinary (head-to-tail) propagating polymer radical has not been found to affect the overall thermal stability.[10,11] The head-to-head radical that results from this process quantitatively rearranges to radicals that are more stable. Thus, the head-to-head structure has not been found in the polymer.

Mechanism of the Thermal Dehydrochlorination of PVC

As we have previously seen, there have been several opinions as to the causes of the rapid thermal degradation of PVC, some of which have been upheld by investigative research and others that still are speculative. The sources of thermal instability now are reasonably well understood, but the degradation mechanism itself still is controversial. An ongoing controversy that is related to this mechanism involves work by W. H. Starnes, Jr. of the College of William and Mary and R. Bacaloglu and M. Fisch of the CK

Witco Corporation. As concluded by Starnes et al., PVC undergoes a thermal dehydrochlorination reaction involving either ion pairs or a four-center transition state with highly polarized C-Cl bonds.[13] The mechanism of the reaction involving ion pairs is shown in Figure 7.

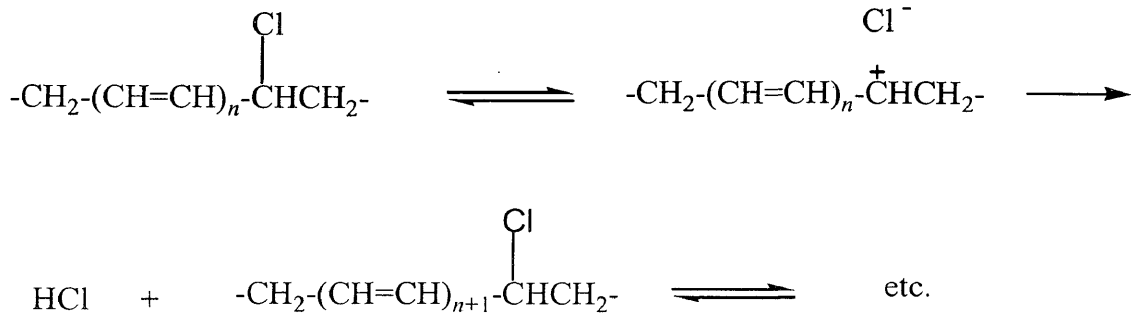


Figure 7. Ion-pair mechanism for the dehydrochlorination of PVC.

Bacaloglu and Fisch have studied the degradation and stabilization of PVC for several years. Their publications give insight into their perspectives on the degradation process and on new methods of stabilization. As discussed in a paper dealing primarily with kinetics, they have proposed that PVC will undergo dehydrochlorination by a mechanism in which an internal alkene or polyene structure rearranges via HCl catalysis at its homochloroallylic end. The resulting structure, which contains an isolated cis double bond, then loses HCl in a six-center concerted process.[8] They believe that this structure is very reactive and that the corresponding trans arrangement does not lose HCl at all because it is thermally stable. They also claim that the degradation does not involve the loss of HCl through the mechanism in Figure 7. Their initially proposed reaction mechanism is shown below in Figure 8.

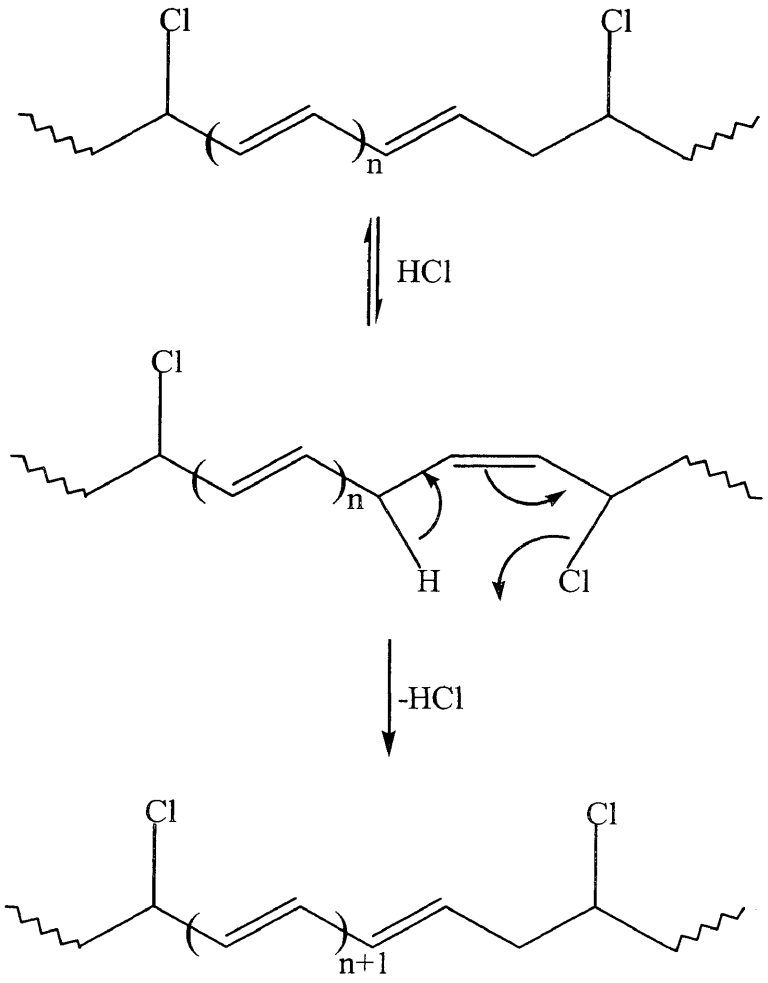


Figure 8. Proposed six-center dehydrochlorination mechanism for PVC.

Starnes et al., tested this mechanism for dehydrochlorination. They synthesized model compounds for chloroallylic and homochloroallylic structures with one double bond, in order to compare their thermal stabilities.[13] The two compounds were heated under argon at 170 °C. After only a few minutes, the compound *trans*-6-chloro-4-decene was still present along with a rearranged product, *trans*-4-chloro-5-decene (Figure 9), and a mixture of dienes formed by dehydrochlorination.

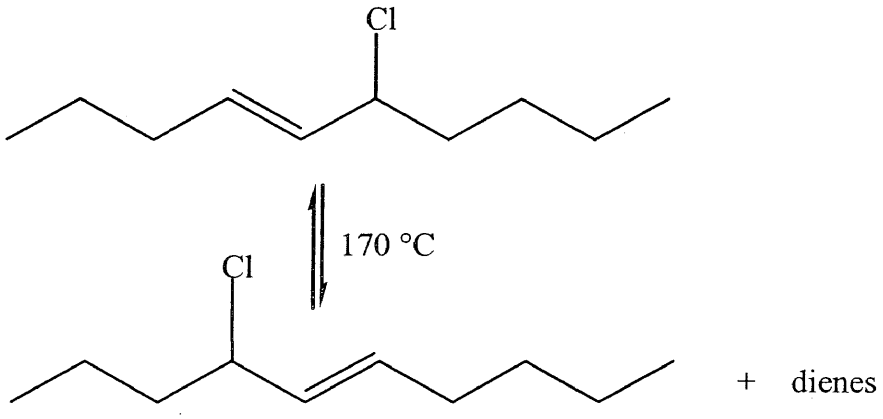


Figure 9. Thermal degradation and rearrangement of 6-chloro-4-decene.

The compound *trans*-9-chloro-6-tridecene, did not react, however, after heating for 24 hours (Figure 10).

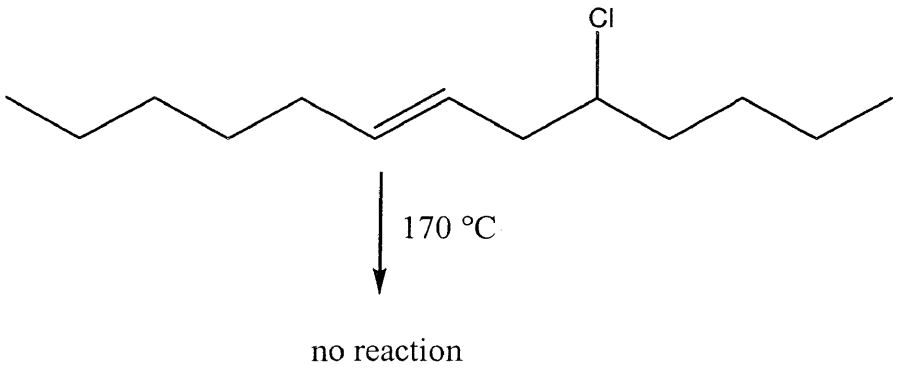


Figure 10. Thermal degradation experiment on *trans*-9-chloro-6-tridecene.

Degradation experiments also were performed with mixtures of the two compounds, so that they would be subjected to the same concentration of HCl. This

procedure caused no significant changes in results. The individual degradation rates of these models can be visualized from Figure 11.[13]

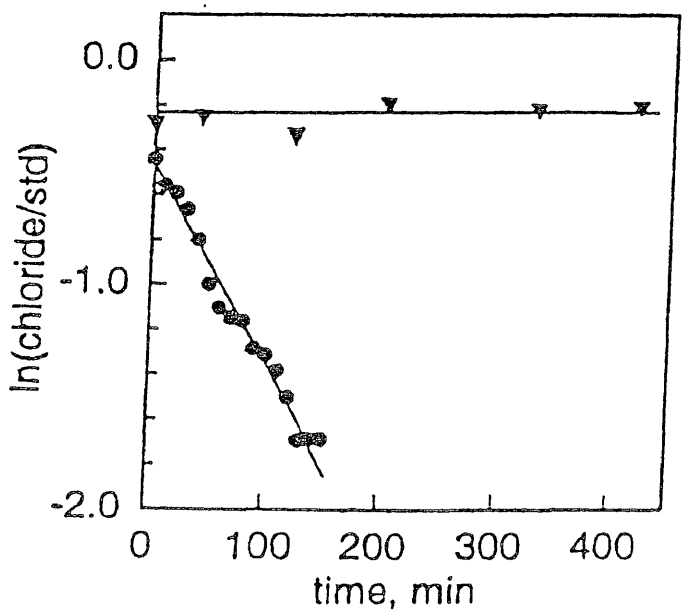


Figure 11. Kinetic plots for the thermal degradation of *trans*-6-chloro-4-decene (•) and *trans*-9-chloro-6-tridecene (▽) at 170 °C.[13]

In a recently published paper, Bacaloglu and Fisch addressed these results and acknowledged that the dehydrochlorination of the allylic chloride is a faster process than the isomerization and subsequent dehydrochlorination of the homoallylic chloride.[14] Thus, they concluded that their mechanism in Figure 8 had been ruled out.

In the same paper, Bacaloglu and Fisch provided information regarding the dehydrochlorination of a *cis*-allylic intermediate.[14] The compounds *trans*-6(4)-chloro-4(5)-tetradecenes were synthesized with the cis isomer making up as little as 4-5% of the product mixture. Upon heating at 150 °C, a temperature at which PVC dehydrochlorinates rapidly, HCl was eliminated, and *trans,trans*- and *cis,trans*-4,6-

tetradecadienes were formed. The concentration of the cis isomer of the starting material increased during the first thirty minutes and then decayed exponentially. Figure 12 shows the concentrations of the four compounds under steady-state conditions.[14]

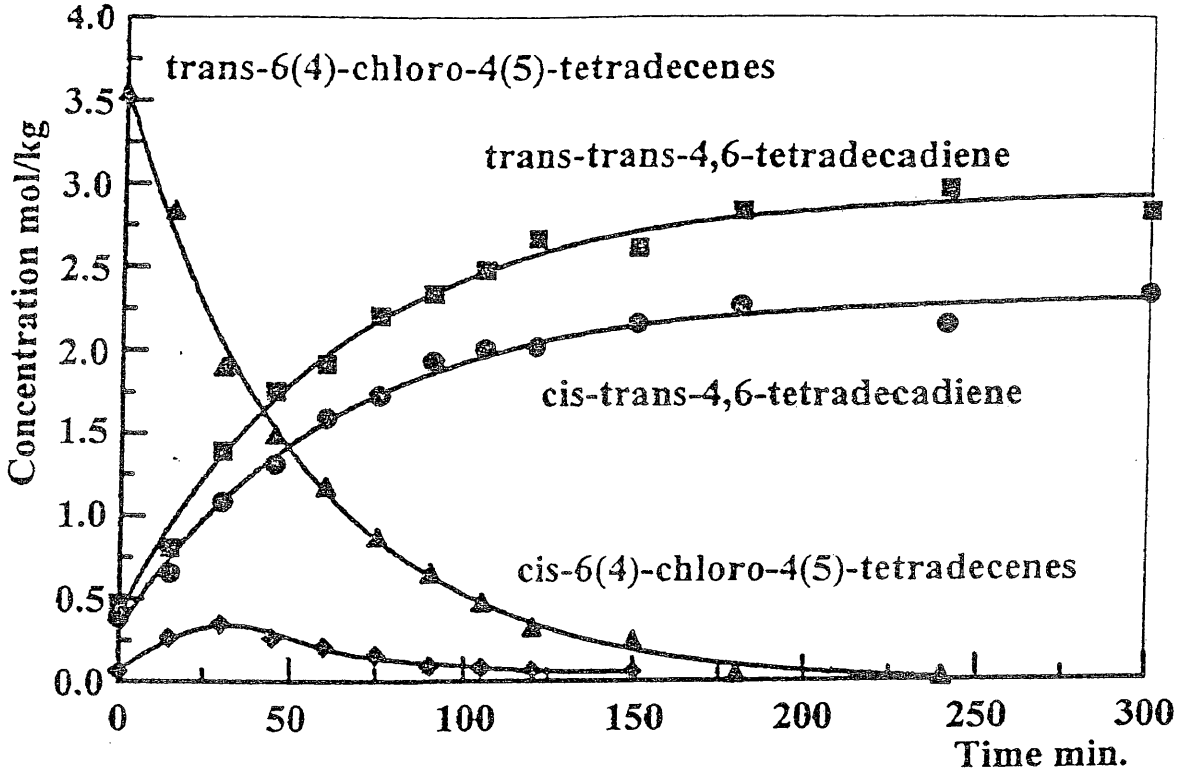
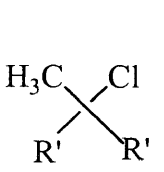


Figure 12. Dehydrochlorination of *trans*-6(4)-chloro-4(5)-tetradecenes at 150 °C.[14]

From these results, the authors concluded that the starting chlorides lose HCl exclusively via the *cis*-allylic chloride in a six-center transition state via a 1,4 elimination.[14] The cis compound was now suggested to result, however, from the 1,3 rearrangement of chlorine at the chloroallylic end. Other reaction schemes were considered, but this mechanism was thought to be the most likely scenario.

In further attempts to investigate the possibility of dehydrochlorination via a four-center transition state or an ion pair, we have performed several experiments. Model compounds that correlate with the thermally unstable structural defects in PVC have been prepared previously in order to compare their degradation rates.[9] A model for the product of a six-center dehydrochlorination, as proposed by Bacaloglu and Fisch, has been made, and a model has now been synthesized for the expected product of a 1,2 dehydrochlorination in the same system. This system consists of a new allylic chloride, which was synthesized and dehydrochlorinated in order to determine both the product(s) and the rate of its degradation.

For obvious reasons, the rate constants for the degradation of individual structural defects in actual PVC samples are very difficult to determine. The reactivity difference between the cis and trans structures of PVC can, however, be related to the reactivities of model compounds. Such model compounds were synthesized earlier in order to obtain their dehydrochlorination rate constants and to learn whether internal allylic, terminal allylic, or tertiary chloride is the main destabilizing contributor. The compounds used for that study are illustrated below and numbered according to the corresponding numbering sequence in the literature.[10]



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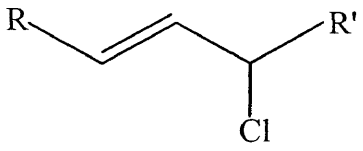

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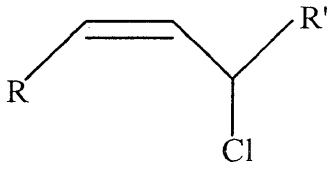

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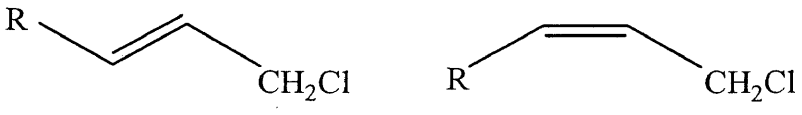
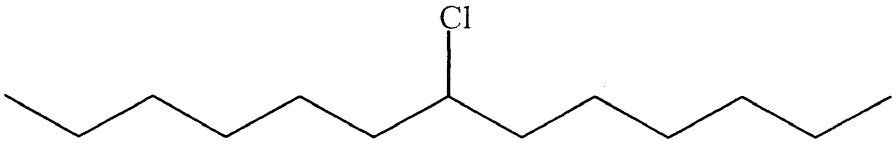


12 **13**



14

R = *n*-Pr; R' = *n*-Bu

Table 1 contains the dehydrochlorination rate constants of these models in two different solvents. Decreasing the argon flow rate increases the steady-state concentration of HCl. Thus the allylic chlorides **10** and **11** are shown to be much more susceptible to HCl catalysis than the tertiary chloride. From this table we also see that there is not much reactivity difference between the cis and trans isomers of the allylic chlorides. This result does not support Bacaloglu and Fisch's theory that a *cis*-allylic chloride is much more reactive than the corresponding trans structure.

Table 1. Dehydrochlorination Rate Constants for Some Models.[10]

model	$k^a \times 10^5$, $(min)^{-1}$ o-$Cl_2C_6H_4$	Ph_2CO
9	780[b]	
	1100	5800
	950[c]	
10	3120[b]	
	600	3300
	290[c]	
11	2000	4900
	860[c]	
12	6	21
13	7	22
14	2	20

[a] At 170±0.5°C with an argon flow rate of 0.14 mL/s unless noted otherwise; reproducibilities were ≤(±7%). [b] Argon flow, ≪0.14 mL/s (too slow for accurate measurement). [c] Argon flow, 1.3 mL/s.

Our present research on the mechanism of the thermal dehydrochlorination of PVC was concerned with the synthesis of the model compounds 3-ethylidenecyclohexene, 1-vinylcyclohexene, and 2-chloro-1-ethylidenecyclohexane. These compounds were useful for exploring the mechanism of thermal HCl loss from PVC containing internal allylic chlorides as structural defects.

2-Chloro-1-ethylidenecyclohexane (a mixture of cis and trans isomers) was synthesized to model internal allylic chloride structures in PVC. When these compounds undergo thermal dehydrochlorination, the 1,2 dehydrochlorination mechanism(s) would lead to the formation of 3-ethylidenecyclohexenes (Figure 13).

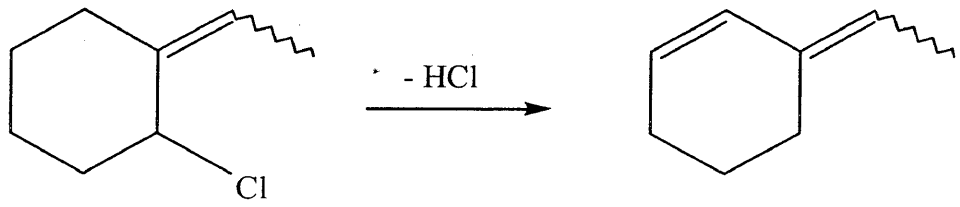


Figure 13. 1,2 Dehydrochlorination of 2-chloro-1-ethylidenecyclohexanes.

On the other hand, the six-center dehydrochlorination mechanism could occur only with the cis isomer and would lead to the formation of 1-vinylcyclohexene (Figure 14).

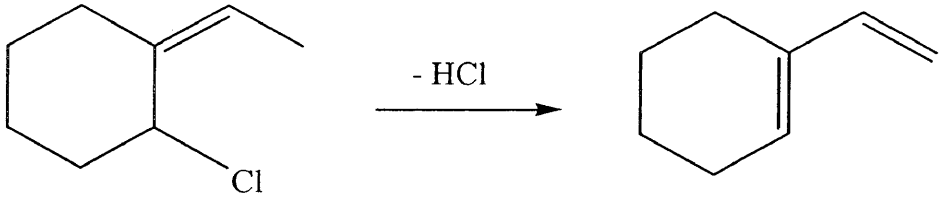


Figure 14. Six-center 1,4 dehydrochlorination of *cis*-2-chloro-1-ethylidenecyclohexane.

However, allylic rearrangement of the starting mixture of chlorides by a 1,3 chloro shift, followed by 1,2 dehydrochlorination, would also produce 1-vinylcyclohexene. Moreover, the latter compound conceivably could undergo HCl-catalyzed isomerization into the 3-ethylidenecyclohexenes. Therefore, conclusive evidence against the occurrence of six-center dehydrochlorination would consist of (a) observation of the reaction in Figure 13 and (b) a conclusive demonstration of the failure

of 1-vinylcyclohexene to rearrange to 3-ethylidenecyclohexenes under the dehydrochlorination conditions.

This thesis presents evidence that argues strongly against the concerted six-center dehydrochlorination of 2-chloro-1-ethylidenecyclohexanes. This evidence, together with the data in Table 1, argues strongly against the new mechanism of Bacaloglu and Fisch.[14] Not only has it been found that *trans*-allylic chlorides are not thermally stable, in opposition to what those workers[14] have concluded, but also the isomerization from trans to cis chlorides has been shown to cause only small changes in the rates of degradation. The new experimental results that do not support concerted six-center dehydrochlorination are reported and discussed in subsequent chapters.

II. EXPERIMENTAL

A. Instrumentation

1. Nuclear Magnetic Resonance (NMR)

The NMR spectra were obtained at normal probe temperature through the use of an Gemini NMR 400 instrument. The chemical shifts are reported in ppm (δ) with TMS (Me_4Si) as an internal reference ($\delta = 0.00$ ppm). The solvent used was chloroform-*d*.

2. Gas Chromatography/Mass Spectroscopy (GC/MS)

The GC/MS data were acquired with a Hewlett-Packard 5890 Series II GC instrument used in conjunction with a 5971A Mass Selective Detector. This apparatus was equipped with an HP-1 capillary column (crosslinked methyl siloxane, with dimensions of 12.5 m x 0.2 mm x 0.33 m). Helium was used as a carrier gas. The GC parameters are listed in Table 2.

Table 2. GC Parameters.

Injector temperature	250 °C
Detector temperature	250 °C
Initial temperature	50 °C
Final temperature	300 °C
Rate	20 °C/min to 300 °C

3. Dehydrochlorination Rates

Samples were titrated with 0.01 M NaOH, using a Metrohm 702 SM Titrino apparatus in order to maintain a constant pH value of 4.30. Samples were thermostated at 170 ± 2°C, and the evolved HCl was swept into deionized water by using an argon flow of 9-10 mL/min.

4. Evaporations

A Buchi Rotavapor was used under aspirator vacuum for the rotary evaporation of ethereal product fractions.

B. Materials

Aldrich was the supplier of 1-acetylcyclohexene (97%), cerium(III) chloride heptahydrate (99.9%), *N*-chlorosuccinimide (98+%), cyclohexanone (99.8%), 1,2-dichlorobenzene (99%), anhydrous DMSO (99.8%), hydrazine monohydrochloride (98+%), hydrogen peroxide (30 wt % solution in water), KO*t*-Bu (95%), anhydrous methyl sulfide (99+%), oxalic acid dihydrate (99%), sodium borohydride (99%), sodium ethoxide (21 wt % solution in ethanol), triethylamine (99.5%), 4-vinylcyclohexene (99%), and 1.0 M vinylmagnesium bromide solution in THF. Fisher supplied Reagent Grade acetaldehyde, acetonitrile, anhydrous magnesium sulfate, chromatographic silica gel (Catalog No. S744-1), potassium bisulfate, ethyl acetate, hexanes, and 4 A molecular sieves.

C. Experimental Procedures

Details of compound characterization appear in the Results chapter.

1. Synthesis of 1-Acetylcyclohexene Oxide[15]

1-Acetylcyclohexene (49.6 g, 0.4 mol) and a 30% aqueous solution of hydrogen peroxide (37 mL, 1.2 mol) in 400 mL of methanol were combined and stirred in an ice bath between 2-5 °C. A 6-M sodium hydroxide solution (33.3 mL, 0.2 mol) was then added dropwise to the mixture in such a manner that the temperature did not rise above 30 °C. The solution was stirred for three additional hours to ensure completion of the reaction. Then the reaction was quenched with 400 mL of deionized water and extracted with two 400-mL portions of ether. After the combined ethereal extracts had been dried over anhydrous $MgSO_4$, the ether was removed at room temperature by rotary evaporation under aspirator vacuum. Presence and purity of the desired product were established by GC/MS data. The epoxide was purified by vacuum distillation at ~5 torr; bp 82 ± 5 °C (lit.[16] bp 86-87 °C at 12 torr); yield, 44.8 g (80%); purity, 95-100%.

2. Synthesis of 2-Ethylidenecyclohexanol[16]

Hydrazine monohydrochloride (0.14 g, 2 mmol) and triethylamine (0.30 g, 3 mmol) in 2 mL of acetonitrile (dried over 4A molecular sieves) were ultrasonicated in a Fisher Scientific FS9 Ultrasonicator for 2 h at room temperature. 1-Acetylcyclohexene oxide (0.09 g, 0.65 mmol) in 1 mL of dry acetonitrile then was added, and the mixture was stirred at room temperature under N_2 for 40-52 h. The progress of the reaction was monitored by GC/MS. When all of the epoxide had

reacted, the reaction was terminated by quenching with a saturated sodium chloride solution (15 mL). The mixture was extracted with two 15-mL portions of ether. Then anhydrous magnesium sulfate was used to dry the combined ethereal layers and the ether was removed by rotary evaporation under aspirator vacuum. The crude allylic alcohol was isolated by chromatography on a 300-mL, 350-mm silica gel column (eluent, hexane-AcOEt : 8-2). Presence and purity of the desired product was determined by GC/MS and NMR data; yield, 0.03 g (35%); purity, 97%.

3. Synthesis of 2-Chloro-1-ethylidenecyclohexane[17]

A solution of *N*-chlorosuccinimide (0.29 g, 2.2 mmol) in anhydrous methylene chloride (10 mL) was cooled to 0 °C in an ice bath under argon. Methyl sulfide (0.15 g, 2.4 mmol) was added dropwise to this solution with stirring. The reaction mixture was cooled to –20 °C prior to the addition of 2-ethylidenecyclohexanol (0.25 g, 2.0 mmol) in methylene chloride (1 mL). After the addition, the reaction mixture was warmed to 0 °C and stirred for an additional hour. The mixture was then poured into an ice-cold sodium chloride solution (10 mL) and extracted with two 4-mL portions of ether. The combined organic layers were washed with two 4-mL portions of cold sodium chloride solution and dried over magnesium sulfate; then the ether was removed by rotary evaporation under aspirator vacuum. The presence of the desired product was established by GC/MS and NMR data; yield, 0.20 g (71%); purity (60%).

4. Thermal Dehydrochlorination of 2-Chloro-1-ethylidenecyclohexane

2-Chloro-1-ethylidenecyclohexane (0.14 g, 1 mmol) was added to 1,2-dichlorobenzene (1.1 mL, 10 mmol), and the solution was heated at 170 ± 2 °C. An

argon stream (9-10 mL/min) was used to sweep the evolved hydrogen chloride into deionized water where it was titrated with a 0.01 M solution of NaOH. The base was introduced via the Metrohm 702 SM Titrino apparatus in order to maintain a constant pH of 4.30. The products of this reaction were analyzed by GC/MS.

5. Synthesis of 3-Ethylidenecyclohexene[18]

4-Vinylcyclohexene (20.0 g, 0.19 mol) and 0.7 M potassium *t*-butoxide in dimethyl sulfoxide (125 mL) were combined and heated to 100 °C with stirring for 75 h. The progress of the reaction was monitored by GC/MS. The resulting solution was quenched with water (100 mL), extracted with two 100-mL portions of ether, and dried over magnesium sulfate. The presence and purity of the expected product was verified by GC/MS data; yield, 6.9 g (35%); purity, 99%.

6. Synthesis of 1-Vinylcyclohexanol[19]

1-Vinylcyclohexanol was formed by allowing cyclohexanone to react with vinylmagnesium bromide in the presence of cerium chloride, a catalyst for the reaction.[19] The cerium chloride (0.56 g, 1.50 mmol) was finely ground into a powder and placed in a flask that then was sealed under vacuum. For two hours the catalyst was heated at 100± 5 °C under vacuum at ~5 torr. Then the temperature was increased to 140 °C under vacuum for two more hours. The flask was filled with argon and immersed in an ice bath between 2-5 °C. Tetrahydrofuran (5 mL), freshly distilled from sodium/benzophenone, was added, and the suspension was vigorously stirred at ambient temperature overnight. The flask was cooled to –78 °C; 0.20 mL (1.50 mmol) of a 1.0-M solution of vinylmagnesium bromide in THF was added with

stirring; the mixture was kept at –78 °C for 1.5 h. Cyclohexanone (0.15 g, 1.0 mmol) was added and allowed to react for one hour, while maintaining a temperature of –78 °C. At this point, the reaction mixture was checked by GC/MS for presence of the alcohol and subsequently treated with 10 mL of 10% acetic acid solution in water. The cooling bath was removed, and the mixture was stirred for 30 min. Then it was extracted with two 25-mL portions of ether, and the ether solution was washed in succession with 10 mL of 10% sodium chloride solution and 10 mL of 10% sodium bicarbonate solution. The ethereal solution was dried over anhydrous magnesium sulfate and subjected to rotary evaporation. The presence of the expected product was verified by GC/MS and NMR data, and the alcohol was isolated by vacuum distillation at ~5 torr; bp 63 ± 2 °C (lit.[20] bp 61 °C at 13 torr); yield, 0.09 g (57%); purity, 97%.

7. Synthesis of 1-Vinylcyclohexene[20]

The isolated alcohol (1.7 g, 13 mmol) synthesized in the above way was combined with 5 wt % of anhydrous potassium bisulfate (0.09 g, 0.66 mmol), and the mixture was heated at 100 °C and stirred for three hours. It then was filtered; the solid was washed with ether (10 mL); and the washings were combined with the original filtrate. Rotary evaporation was used to remove the ether, and the product was analyzed by GC/MS; yield, 1.20 g (71%); purity, 61%.

III. RESULTS

Model Compound for the Internal Allylic Structure in PVC

Two possible synthetic routes leading to a model compound (**4**) for the internal allylic structure in PVC are shown in Figure 15.

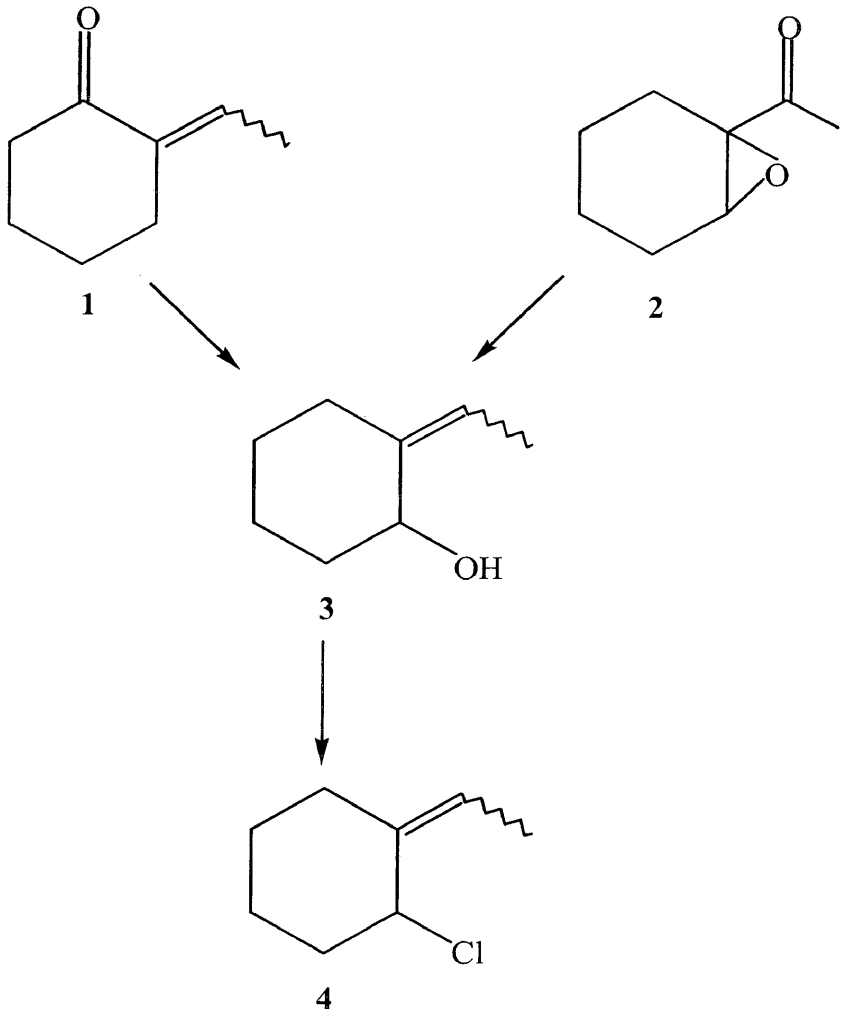


Figure 15. Synthesis of 2-chloro-1-ethylidenecyclohexanes.

One route required the preliminary synthesis of 2-ethylidenecyclohexanone (**1**).[21] The carbonyl group of this compound was to be reduced to a hydroxyl group in order to form **3**. Cyclohexanone and sodium ethoxide (21 wt % in ethyl alcohol) were combined with stirring and cooling to 0 °C. A solution of acetaldehyde in cyclohexanone was then added slowly, and the mixture was stirred for an additional 45 minutes. Addition of water and treatment with oxalic acid dihydrate, followed by a conventional aqueous workup, gave a product mixture that was subjected to vacuum distillation in a spinning band micro still with a nominal separation efficiency of 150 theoretical plates. Vacuum distillation was the method of separation used by Van-Catledge et al., and the yield they reported for **1** was 26%.[21] An easier and more effective method of separation may be column chromatography, but this method was never tried. Despite considerable difficulties encountered with the distillation, we eventually isolated the compound in very low yields with a purity of 95% and then reduced it to compound **3** having a purity of 81%.

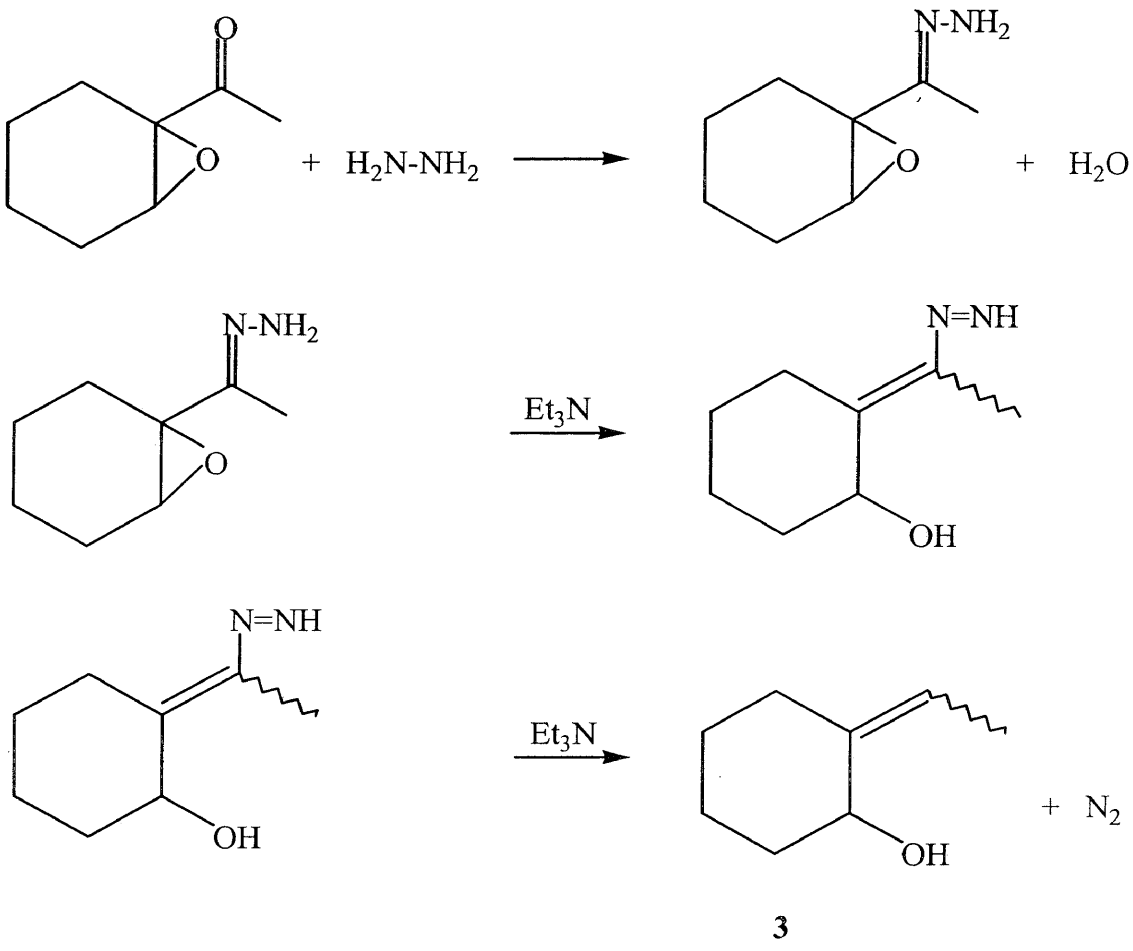
The method used for the reduction was as follows.[22] Compound **1** (1 mmol) and cerium(III) chloride heptahydrate (1 mmol) were dissolved in methanol. Sodium borohydride (1 mmol) was added with stirring, which was continued for 1 hour. (Cerium(III) chloride heptahydrate was used to form a complex reagent to prevent the formation of alkoxyborohydrides from the methanol and $NaBH_4$.) After neutralization with dilute aqueous HCl and a standard aqueous workup, crude **3** (identified by GC/MS) was obtained in low yield. Because of the small amount of alcohol formed, the conversion of this product into **4** was not attempted. Following several unsuccessful

attempts to prepare a useful amount of purified **1**, an alternative method of synthesis was chosen.

The second method for the synthesis of **3** required the preparation of 1-acetylcyclohexene oxide (**2**), which was subsequently converted into the desired alcohol. The synthesis of **2** was patterned after a similar synthesis published in *Organic Syntheses.*[15] The results were checked by GC/MS analysis (Figures 1-1 and 1-2). The retention time of **2** was 3.44 min, and after vacuum distillation, a purity of 95-100% was obtained. The mass spectrum of this compound is shown in Figure 1-1. It shows $M^{+\bullet}$ = 140, as required. Figure 1-2 shows the mass spectrum of a minor impurity typically present and difficult to separate from the epoxide. The retention time of this impurity is 3.71 min and it apparently has $M^{+\bullet}$ = 156 (very weak). It appears that the impurity may have resulted from the base-promoted addition of methanol to the alkene double bond of 1-acetylcyclohexene.

After purification, **2** was converted into **3** by a process known as the Wharton transposition, which enables the formation of allylic alcohols from acyl epoxides, via α,β–epoxyhydrazones.[16] This reaction requires anhydrous hydrazine, which was formed by the ultrasonication of triethylamine and hydrazine monohydrochloride. The ultrasonication helps to establish the equilibrium shown in Figure 16, which is shifted to the right by using an excess of triethylamine. The suggested mechanism of the Wharton transposition is shown in Figure 17.

Figure 16. Formation of hydrazine.



3

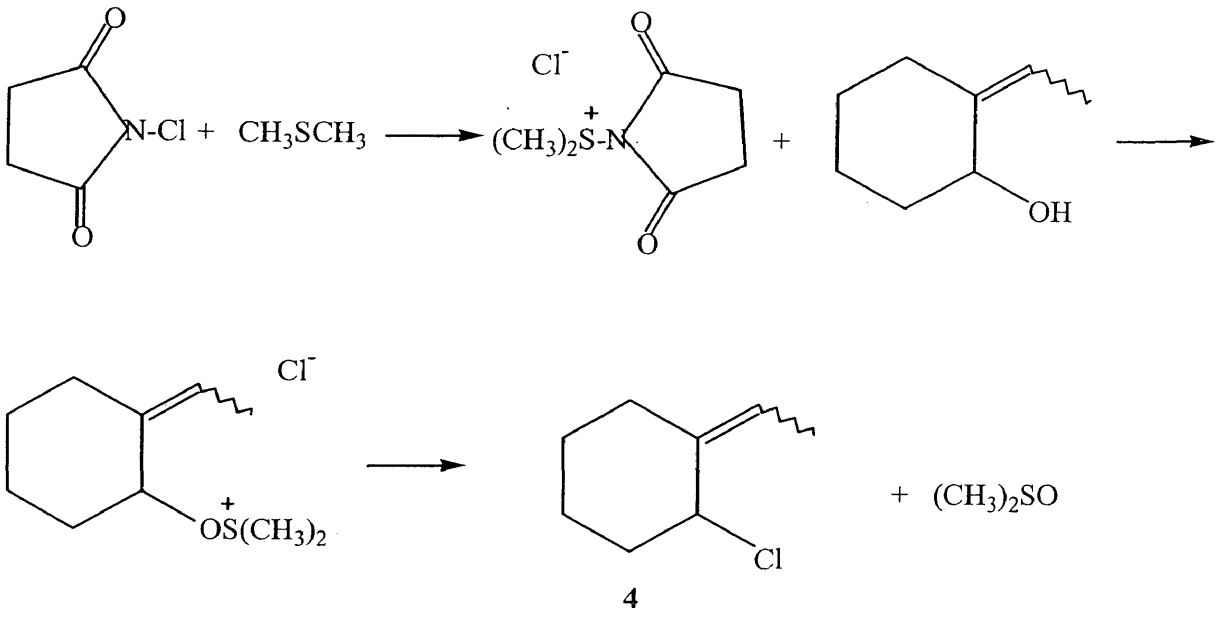
Figure 17. Synthesis of 2-ethylidenecyclohexanols.

The results of this reaction were determined by GC/MS analysis, which showed that the purity of the crude alcohol product (**3**) was never greater than 50%. The GC/MS results after 48 h of reaction are shown in Figures 2-1 through 2-5. In the mass spectra, the two peaks with retention times of 0.37 and 0.40 min are due to residual hydrazine and acetonitrile. Compound **3** ($M^{+\bullet}$= 126) occurs as two stereoisomers with very similar mass spectra (Figures 2-1 and 2-2) and retention times of 2.91 and 3.05 min. The component with a retention time of 3.22 min and $M^{+\bullet}$= 124 is apparently an isomer of 1-

acetylcyclohexene. Figures 2-4 and 2-5 show the mass spectra of two other unidentified by-products that had retention times of 5.05 and 9.41 min.

Isolation of **3** was performed by using column chromatography. The column was packed with silica gel, and an 8:2 (v/v) mixture of hexane:ethyl acetate was used as the eluent. The GC/MS results for the purified alcohol stereoisomers are shown in Figures 3-1 and 3-2. The retention times of 0.47 and 0.62 in these figures are for the components of residual eluent. Figures 3-3 and 3-4 show the ^{1}H and ^{13}C NMR spectra, which are in very good agreement with the spectra reported for **3** in the literature.[16,23] Distorted singlets (actually triplets) present in the ^{1}H spectrum at 4.1 and 4.8 ppm correspond to the C<u>H</u>OH proton of the trans and cis isomers, respectively.[23] Additional absorption occurs between 1.2 and 2.6 ppm, owing to the presence of residual eluent. The unassigned peaks in the ^{13}C spectrum are thought to be due in part to residual eluent and partly to multiplicity resulting from the presence of the chiral <u>C</u>HOH carbon.

Compound **3** was converted into chloride **4** via a method utilized by Corey et al.,[17] in which the replacement of the hydroxyl group by chlorine is done under neutral conditions (see Figure 18). The alcohol reacts with the complex formed from *N*-chlorosuccinimide and methyl sulfide in order to produce **4.**



4

Figure 18. Synthesis of 2-chloro-1-ethylidenecyclohexanes.

The presence of **4** was verified by GC/MS (Figures 4-1 through 4-5) and NMR analysis (Figure 4-6). The $M^{+\bullet}$ values of this product are 144 and 146 in a ratio of 3:1, respectively. Three isomers of the compound sometimes appeared in the gas chromatograph. Two are believed to be the stereoisomers of **4**, while the other is considered to be the product of an allylic rearrangement. The retention times of the three isomers are 3.18, 3.29, and 3.33 minutes. It is not yet entirely clear which of these compounds is which.

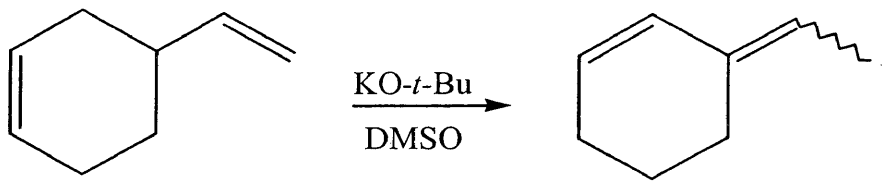
Dehydrochlorinated product isomers (dienes) appeared in the GC/MS traces as well. It was uncertain whether the thermally unstable chlorides degraded after injection into the GC/MS apparatus or simply upon exposure to atmospheric conditions. The degradation products had retention times of 1.97 and 2.07 min and the expected $M^{+\bullet}$ value of 108. Their mass spectra are shown in Figures 4-1 and 4-2.

Figure 4-6 shows the ^{13}C NMR results. This spectrum strongly suggests the absence of significant amounts of dehydrochlorination products from the original mixture of allylic chlorides.

The mixture of chlorides was thermally dehydrochlorinated at 170 ± 2 °C. After 50 minutes, the extent of dehydrochlorination was calculated to be 72.6%, and two isomeric dienes were formed. Figures 5-1 and 5-2 show their mass spectra. The rate constant for the initial stage of dehydrochlorination was estimated to be ca. 4.3 x 10^{-2}/min from the slope of the plot in Figure 5-3. Figure 5-4 shows a plot of [ln a/(a-x)] vs. time, where a = the initial amount of **4,** and x = the total amount of NaOH used in the titration. This crude first-order plot gave a rate constant of ca. 2.3 x 10^{-2}/min. Both rate constants are similar to values reported previously for **10** and **11** in *o*-dichlorobenzene (see Table 1).

Models for the Possible Thermal Dehydrochlorination Products of 4

The base-catalyzed isomerization of 4-vinylcyclohexene in the presence of 0.7 M potassium *t*-butoxide in DMSO was conducted in order to synthesize the cis and trans isomers of **5**.[18]



5

Figure 19. Synthesis of 3-ethylidenecyclohexenes.

After the reaction, the product mixture usually contained up to 97% of compound **5**. As noted in the published procedure,[18] purification of **5** was attempted by fractional distillation under atmospheric pressure. However, when this purification method was tried, the purity of **5** decreased. Heating promoted the formation of by-products and resulted in poor separation. The GC/MS results for the product formed prior to distillation are shown in Figure 6-1.

The synthesis of diene **7** first required the preparation of 1-vinylcyclohexanol, (**6**). This compound was then dehydrated to form **7**.

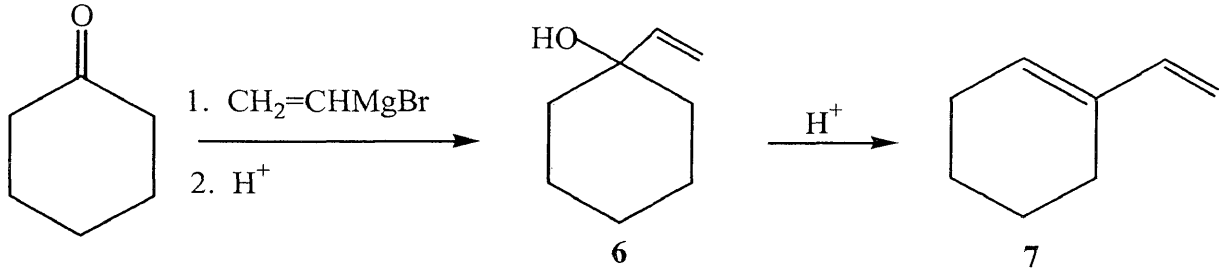


Figure 20. Synthesis of 1-vinylcyclohexene.

The first attempt at the formation of the alcohol was unsuccessful for producing a large yield of product. Under nitrogen, vinylmagnesium bromide was added dropwise to cyclohexanone. During the addition, the temperature was kept at or below 35 °C. Stirring was continued for 30 minutes upon completion of the addition, and the mixture then was refluxed for one hour. A saturated solution of ammonium chloride was slowly added. Ether was used to extract the organic layer, which was subsequently dried over magnesium sulfate and subjected to rotary evaporation in order to remove the ether. Analysis by GC/MS showed that cyclohexanone comprised a large part of the residue.

Vacuum distillation through a Vigreux column was attempted, and when this method of separation did not succeed, the spinning band microstill was used. The results of the separation still were poor. The major difficulty was the unsatisfactory separation of the 1-vinylcyclohexanol from the cyclohexanone.

The second method used for the synthesis of **6** involved the reaction of cyclohexanone with vinylmagnesium bromide in the presence of cerium(III) chloride. From the experimental results published by Imamoto et al., it is seen that when the reaction was performed without cerium chloride, a 30% yield was obtained for the alcohol addition product and a 35% yield for the ketol product shown in Figure 21.[19]

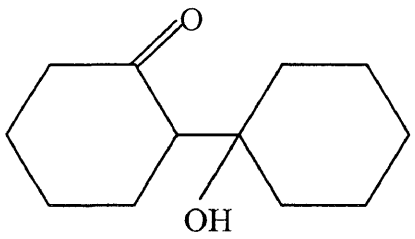


Figure 21. Side product formed during reaction of Grignard reagent and cyclohexanone.

When cerium(III) chloride was used in the reaction, the yield of **6** increased to 80%, and no ketol product was formed.[19] This reaction must be performed at very low temperatures (–78 °C was used by us). At 0 °C, vinylic Grignard reagents will decompose upon interaction with cerium(III) chloride.[19]

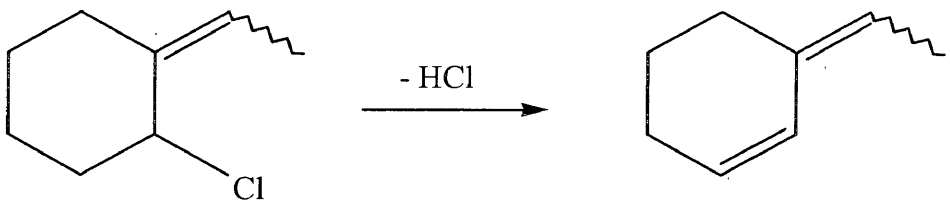
The GC/MS results for the synthesis of compound **6** are shown in Figures 7-1 and 7-2. Figure 7-1 shows the mass spectrum of a minor by-product, which has a retention time of 1.51 min. The retention time of 1-vinyl-1-cyclohexanol ($M^{+\bullet}$ = 126) is 2.25 min,

as shown in Figure 7-2. The ^{1}H NMR spectrum of this alcohol, shown in Figure 7-3, has a peak between 3.3 and 3.5 ppm resulting from the proton of the hydroxyl group. Peaks present at 5.0, 5.2, and 6.0 ppm are due to the protons of the vinyl group. Figure 7-4 is the ^{13}C NMR spectrum.

After fractional vacuum distillation of the reaction products, the isolated portion of **6** was dehydrated to compound **7** upon addition of potassium bisulfate. The GC/MS results for the product mixture are shown in Figures 8-1 through 8-5. Compound **7** has a retention time of 1.72 min and its mass spectrum (Figure 8-1) differs considerably from the dehydrochlorination product spectra shown in Figures 5-1 and 5-2. The ^{13}C NMR spectrum (not shown) of the product mixture was complex but, significantly, did not contain any resonances near 12 ppm, which is the region where the methyl peak of *cis*- and *trans*-**5** would have appeared.

IV. DISCUSSION AND CONCLUSIONS

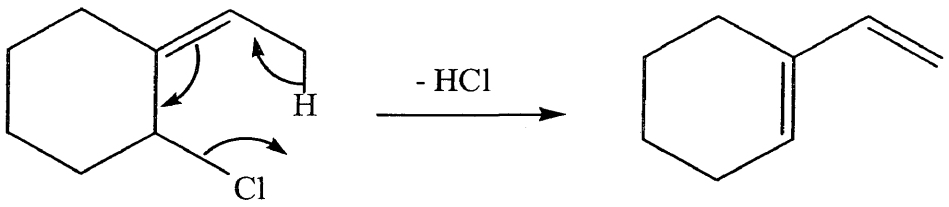
2-Ethylidenecyclohexanol was prepared and converted into 2-chloro-1-ethylidenecyclohexane (**4**). This compound (actually an isomer mixture), which models the internal chloroallylic structure in PVC, was synthesized in order to measure its rate of dehydrochlorination and to determine whether its major degradation product consists of 3-ethylidenecyclohexenes or 1-vinylcyclohexene. The products expected via the 1,2 loss of HCl are 3-ethylidenecyclohexenes (**5**), as shown in Figure 22.



4 **5**

Figure 22. Formation of 3-ethylidenecyclohexenes through a 1,2 dehydrochlorination mechanism.

If the reaction were to proceed through the six-center 1,4 process that Bacaloglu & Fisch[14] would expect, the dehydrochlorination product would be 1-vinylcyclohexene (**7**), as illustrated in Figure 23.



7

Figure 23. Formation of 1-vinylcyclohexene through a six-center 1,4 dehydrochlorination mechanism.

The gas chromatogram of compound **5** obtained from the isomerization of 4-vinylcyclohexene shows that **5** has a retention time that is extremely close to the retention times of the dienes formed by dehydrochlorination. Those two isomers have retention times of 1.96 and 2.07 min, while the retention time of the isomerization product is 2.00 min. Thus the dehydrochlorination appears to have occurred via the 1,2 mechanism shown in Figure 22. Dehydrochlorination through the 1,4 mechanism shown in Figure 23 does not appear to have occurred to any significant extent. If HCl had been lost through that mechanism, a diene peak for **7** with a retention time of 1.72 min and a mass spectrum like that of Figure 8-1 would have been observed. Acid-catalyzed isomerization of **7** into **5**, under the dehydrochlorination conditions, has not yet been ruled out by experimentation. However, this isomerization would have had to occur quantitatively in order to account for the apparently exclusive formation of **5** from **4**.

All of the evidence now available strongly suggests, therefore, that the new six-center mechanism[14] for the dehydrochlorination of secondary allylic chlorides is inoperative.

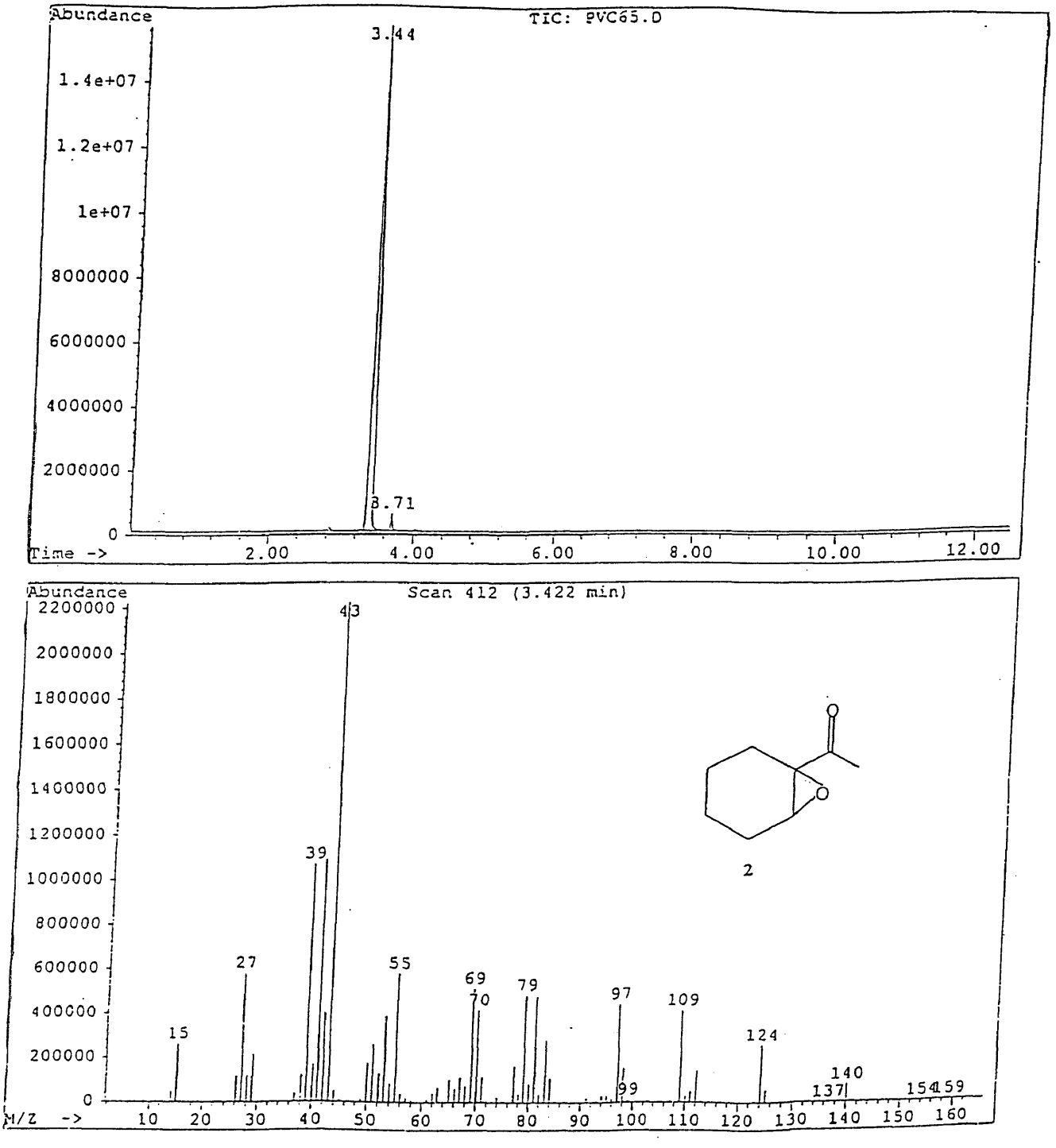


Figure 1-1. GC/MS analysis of 1-acetylcyclohexene oxide (**2**).

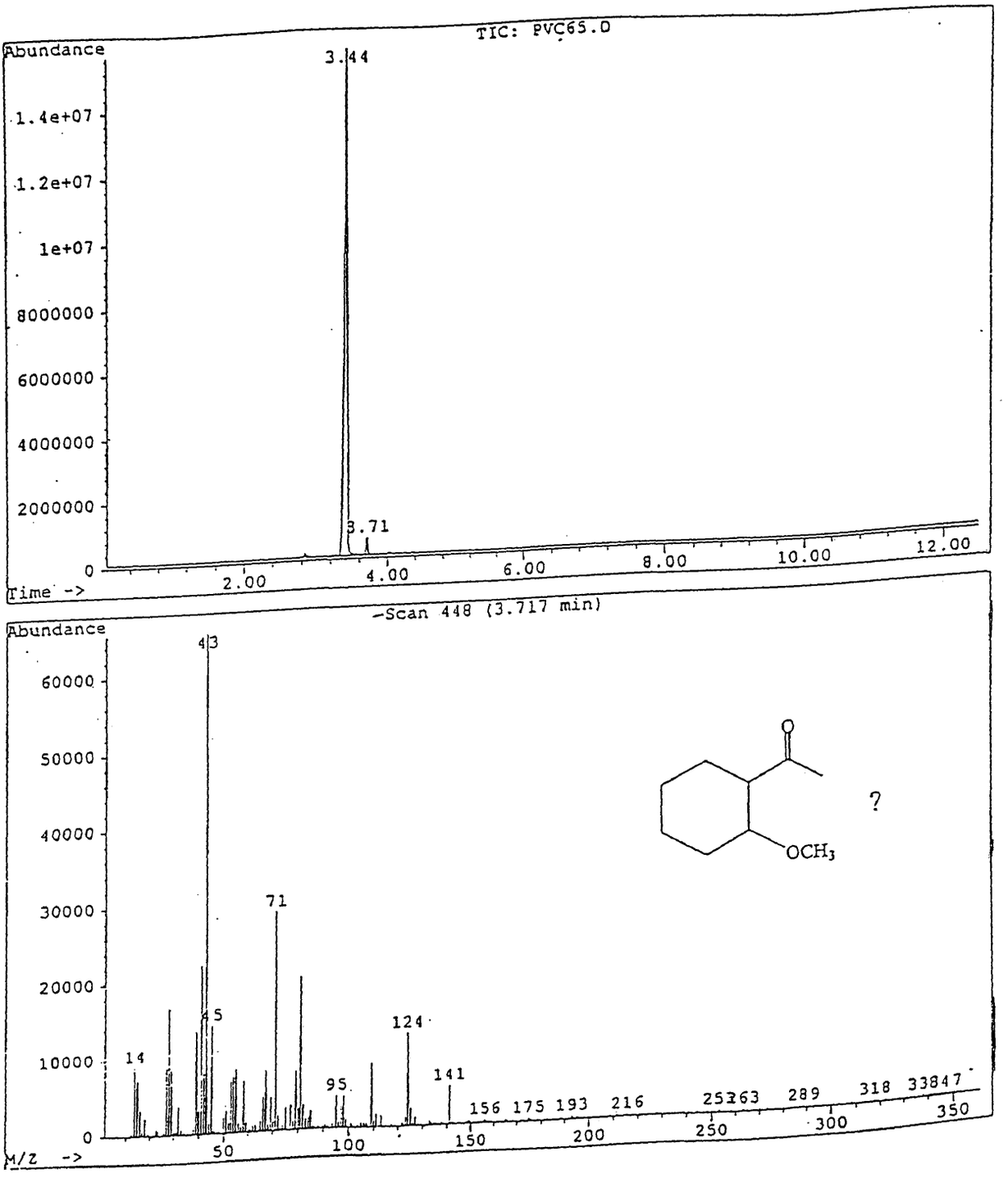


Figure 1-2. Impurity in compound **2**.

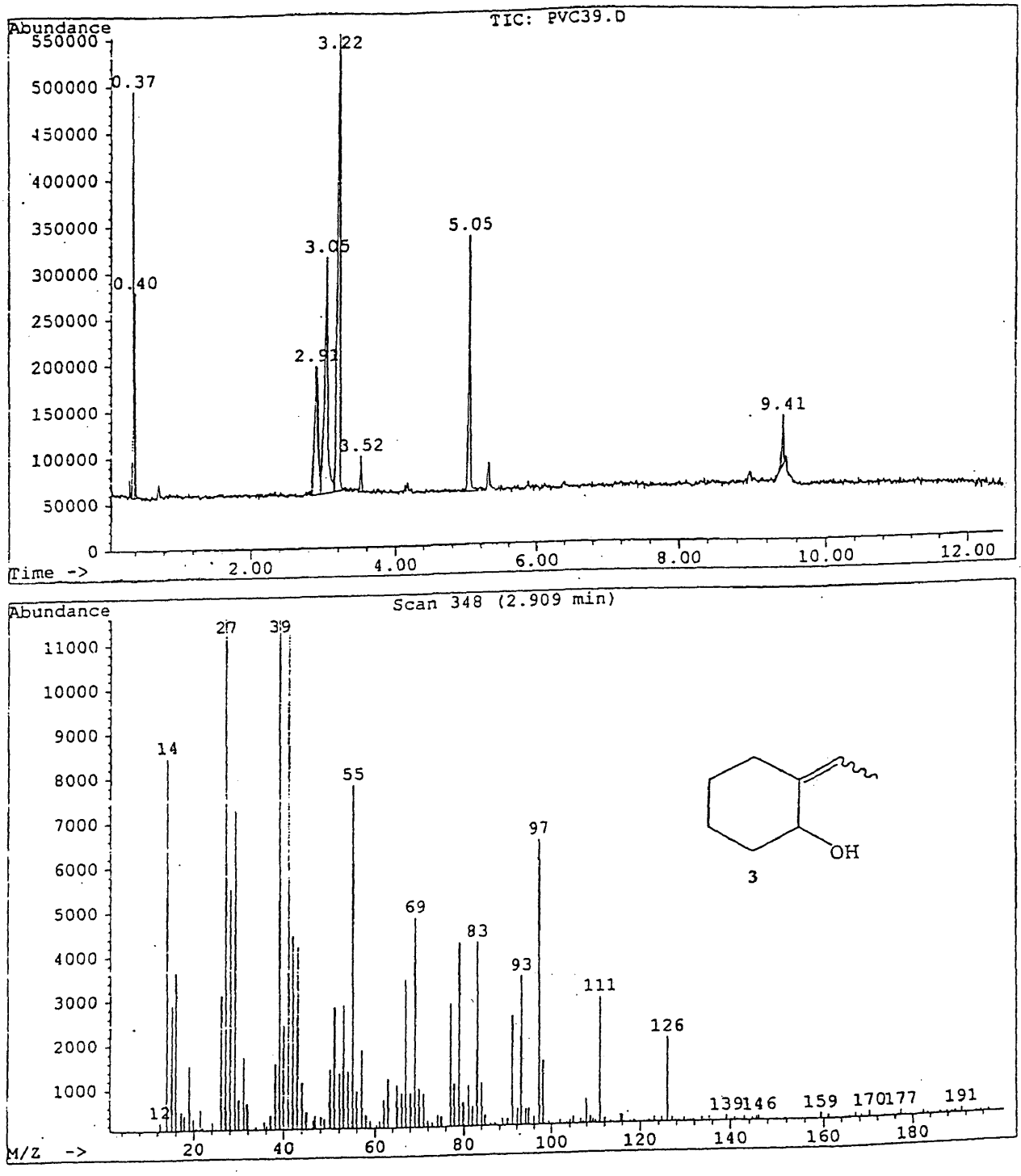


Figure 2-1. GC/MS analysis of Wharton transposition product after 48 h.

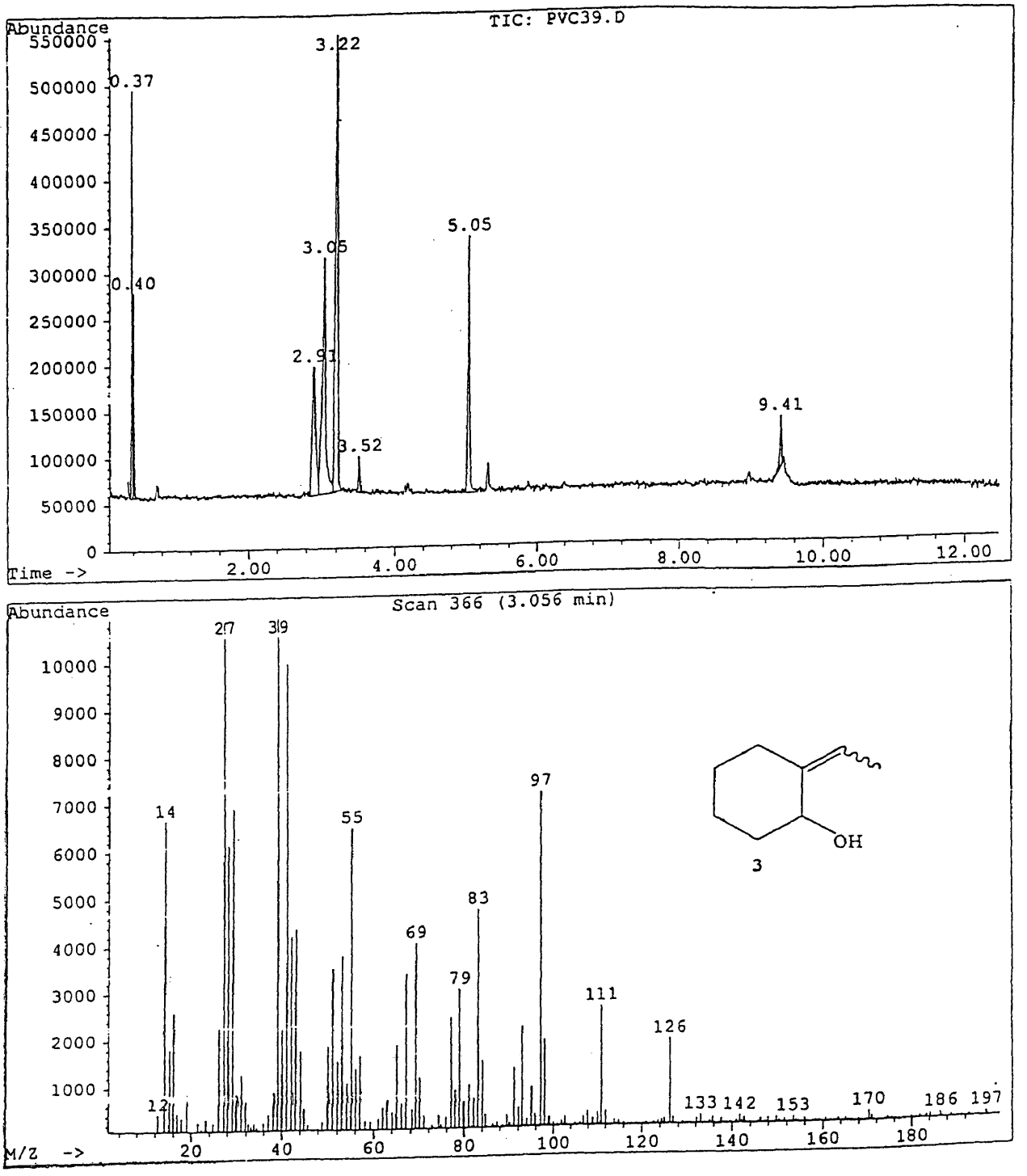


Figure 2-2. GC/MS analysis of Wharton transposition product after 48 h.

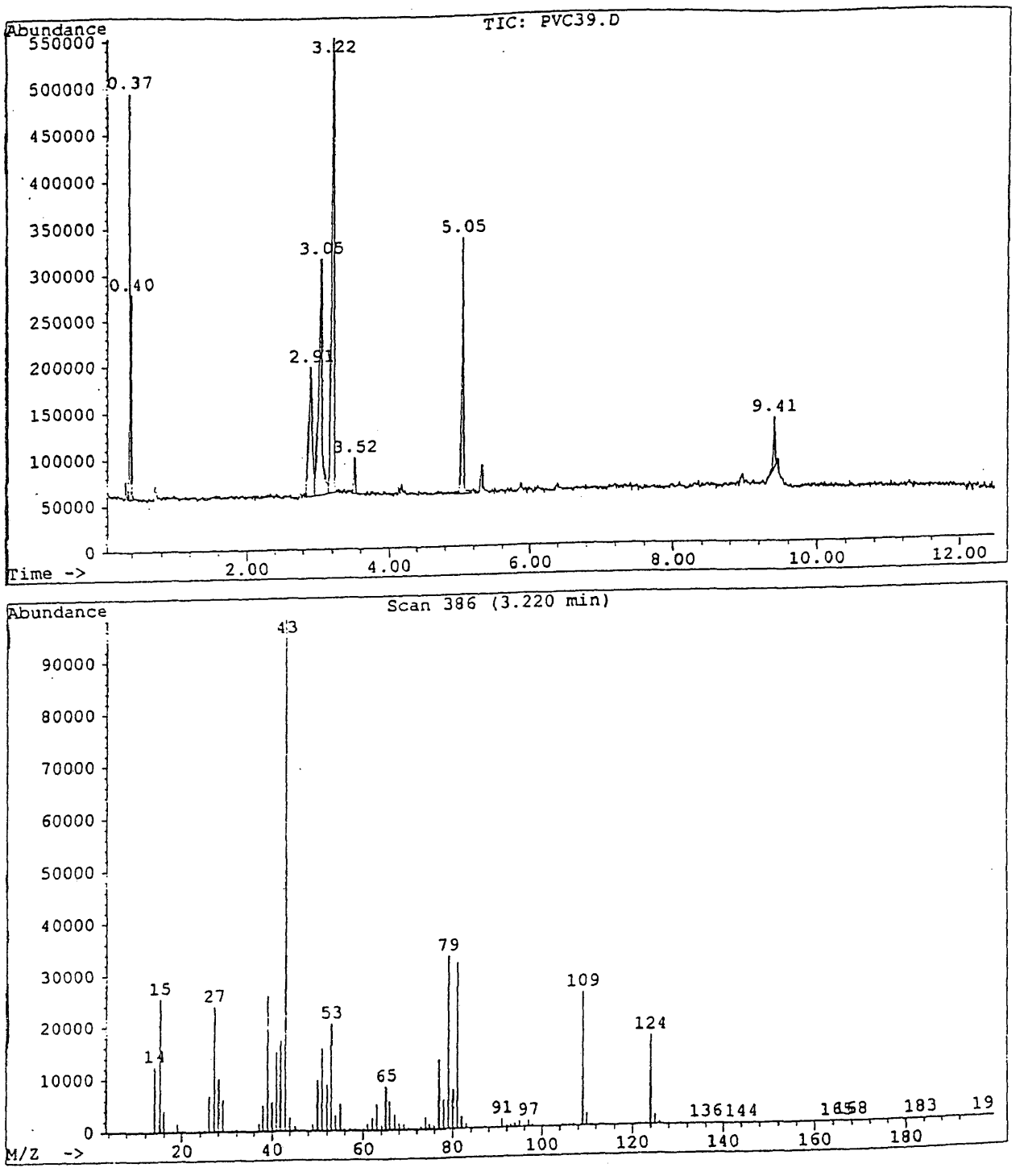


Figure 2-3. GC/MS analysis of Wharton transposition product after 48 h.

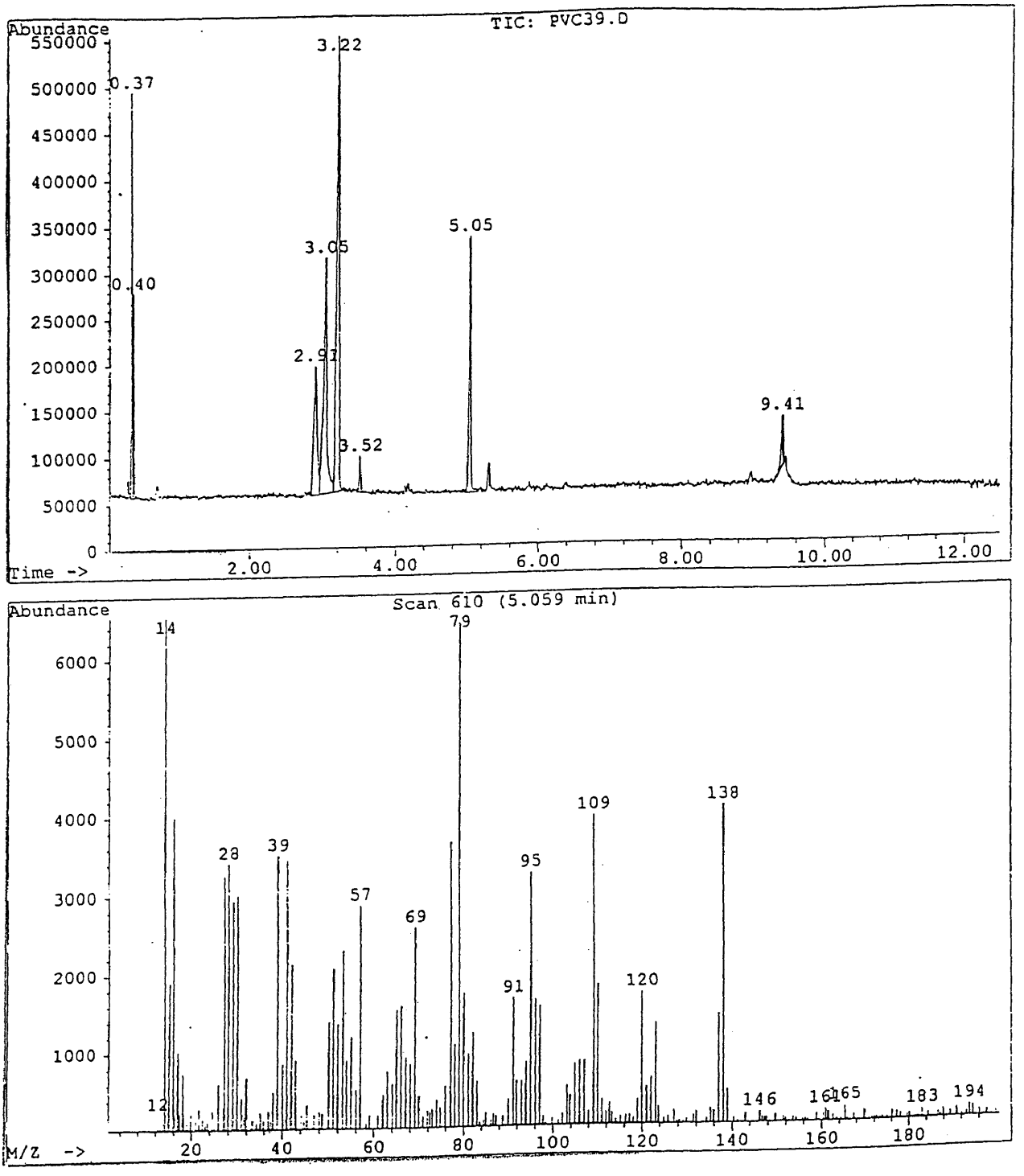


Figure 2-4. GC/MS analysis of Wharton transposition product after 48 h.

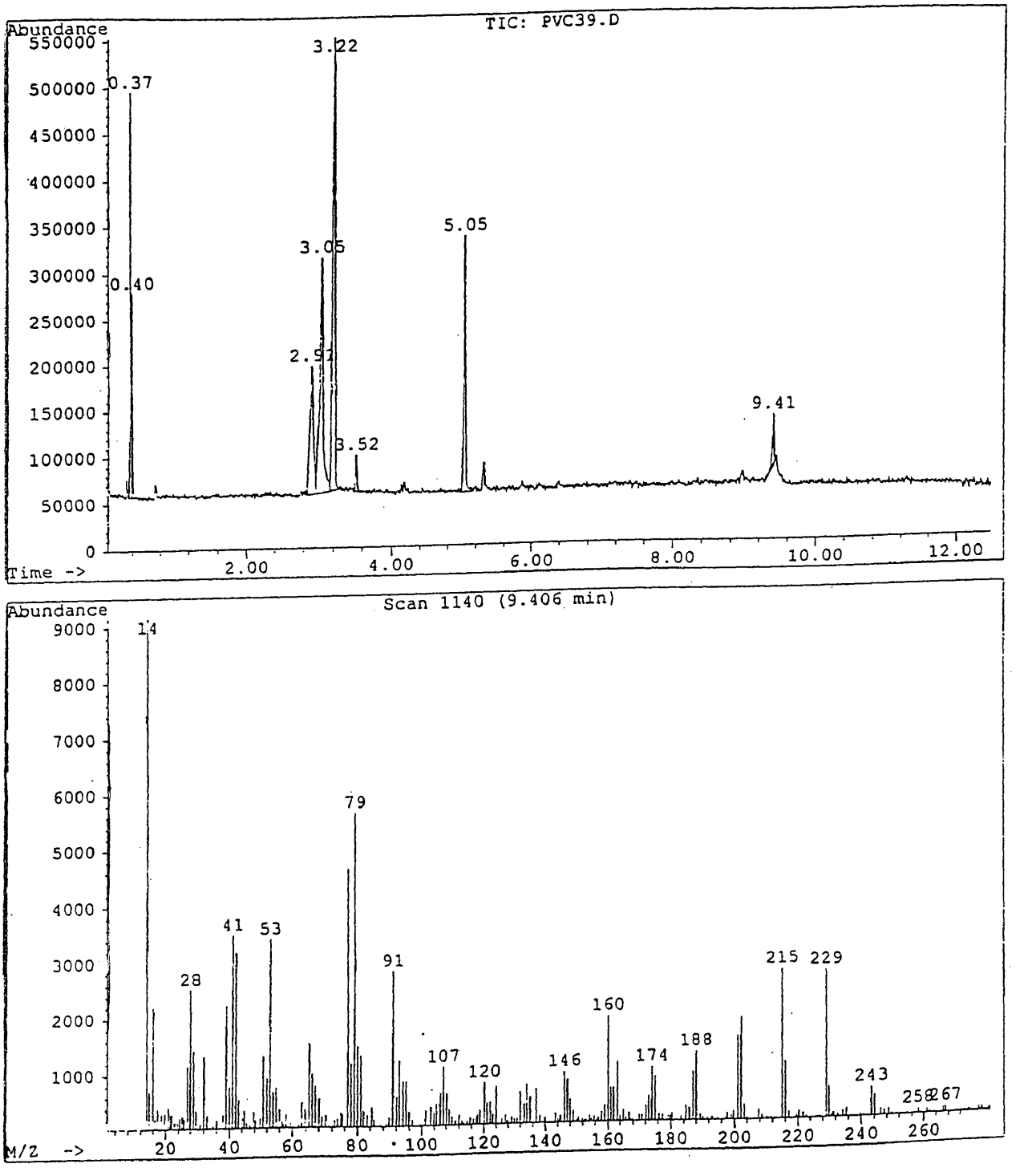


Figure 2-5. GC/MS analysis of Wharton transposition product after 48 h.

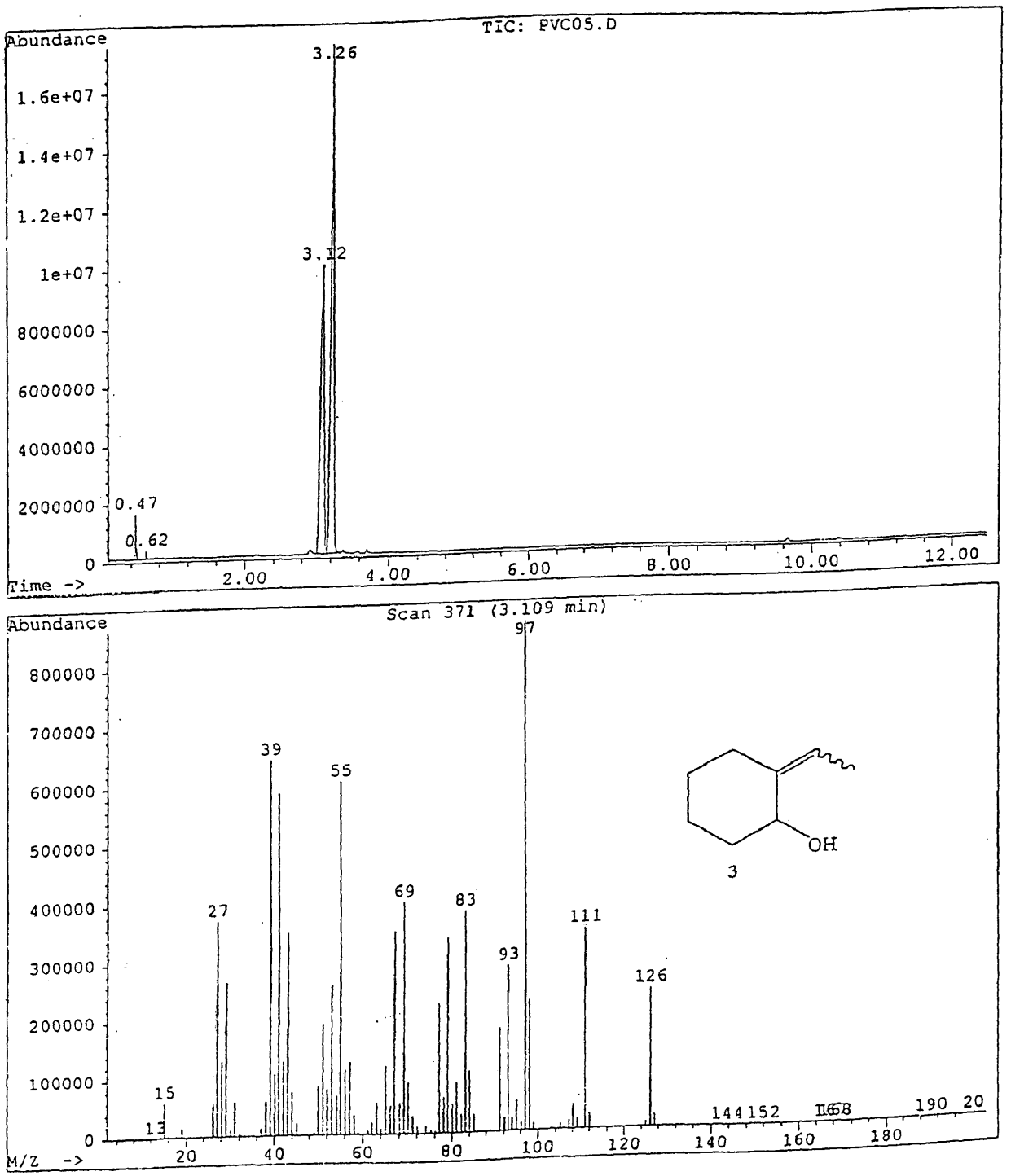


Figure 3-1. GC/MS analysis of 2-ethylidenecyclohexanol purified by column chromatography.

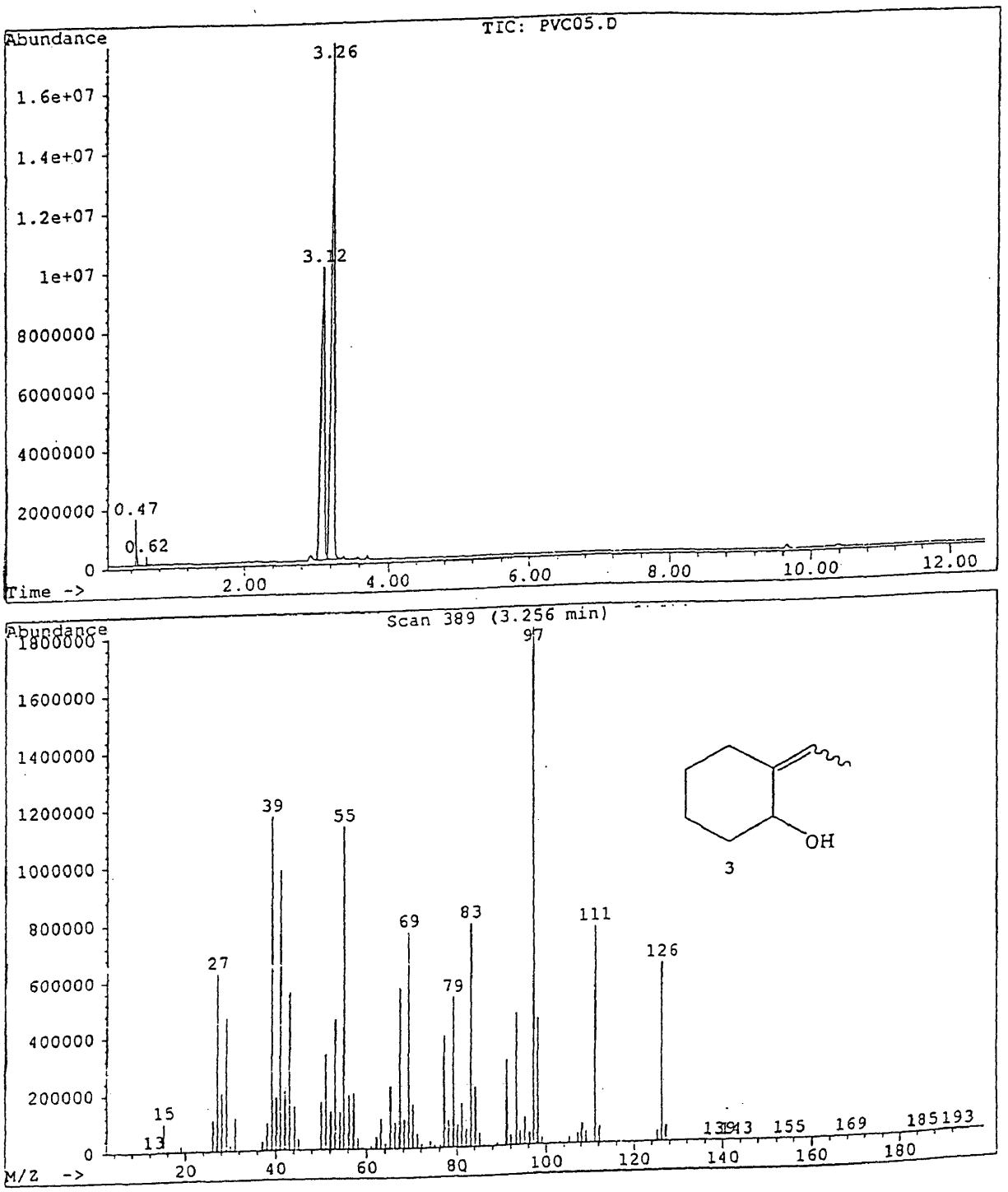


Figure 3-2. GC/MS analysis of 2-ethylidenecyclohexanol purified by column chromatography.

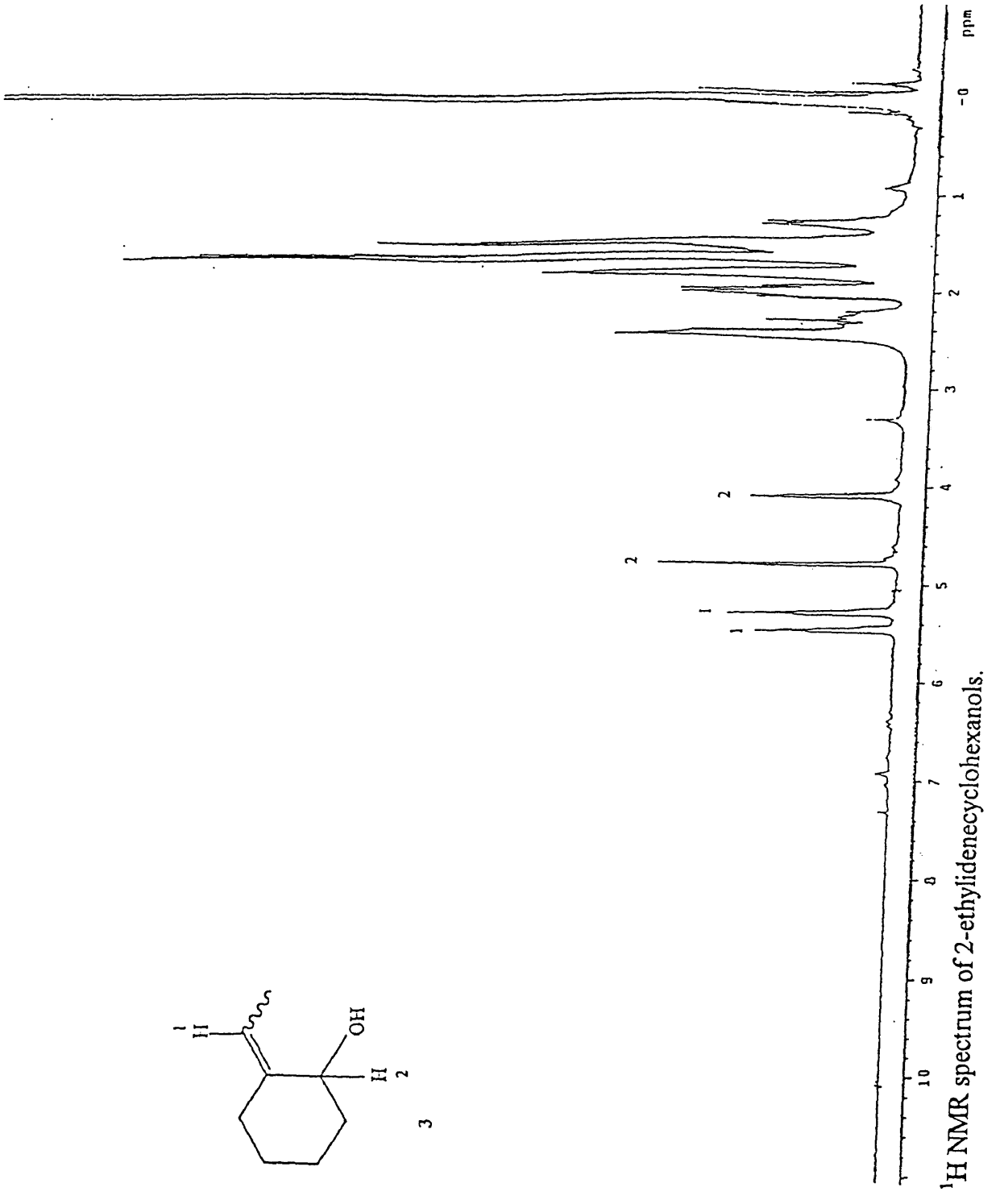


Figure 3-3. ^{1}H NMR spectrum of 2-ethylidenecyclohexanols.

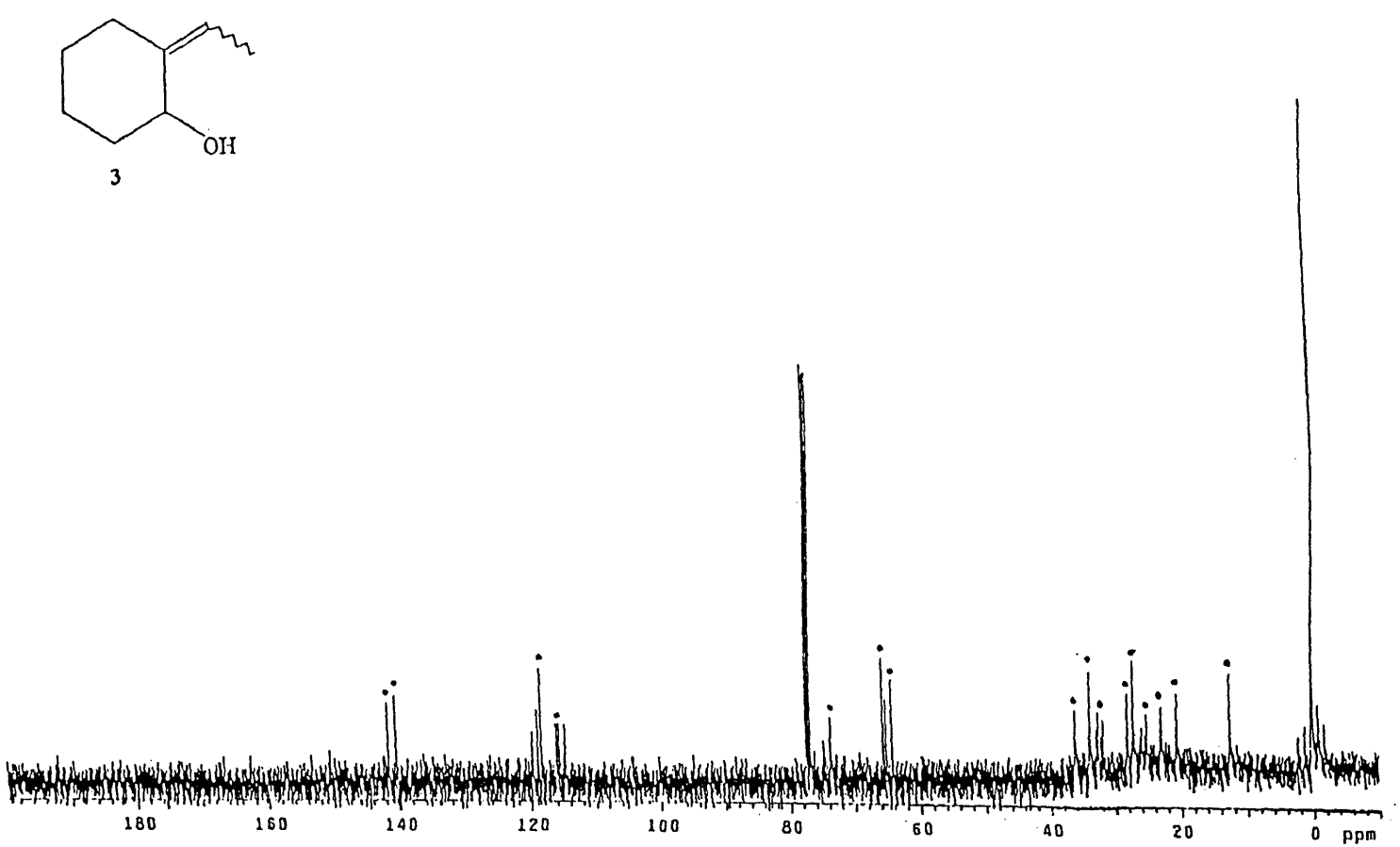


Figure 3-4. ^{13}C spectrum of 2-ethylidenecyclohexanols.

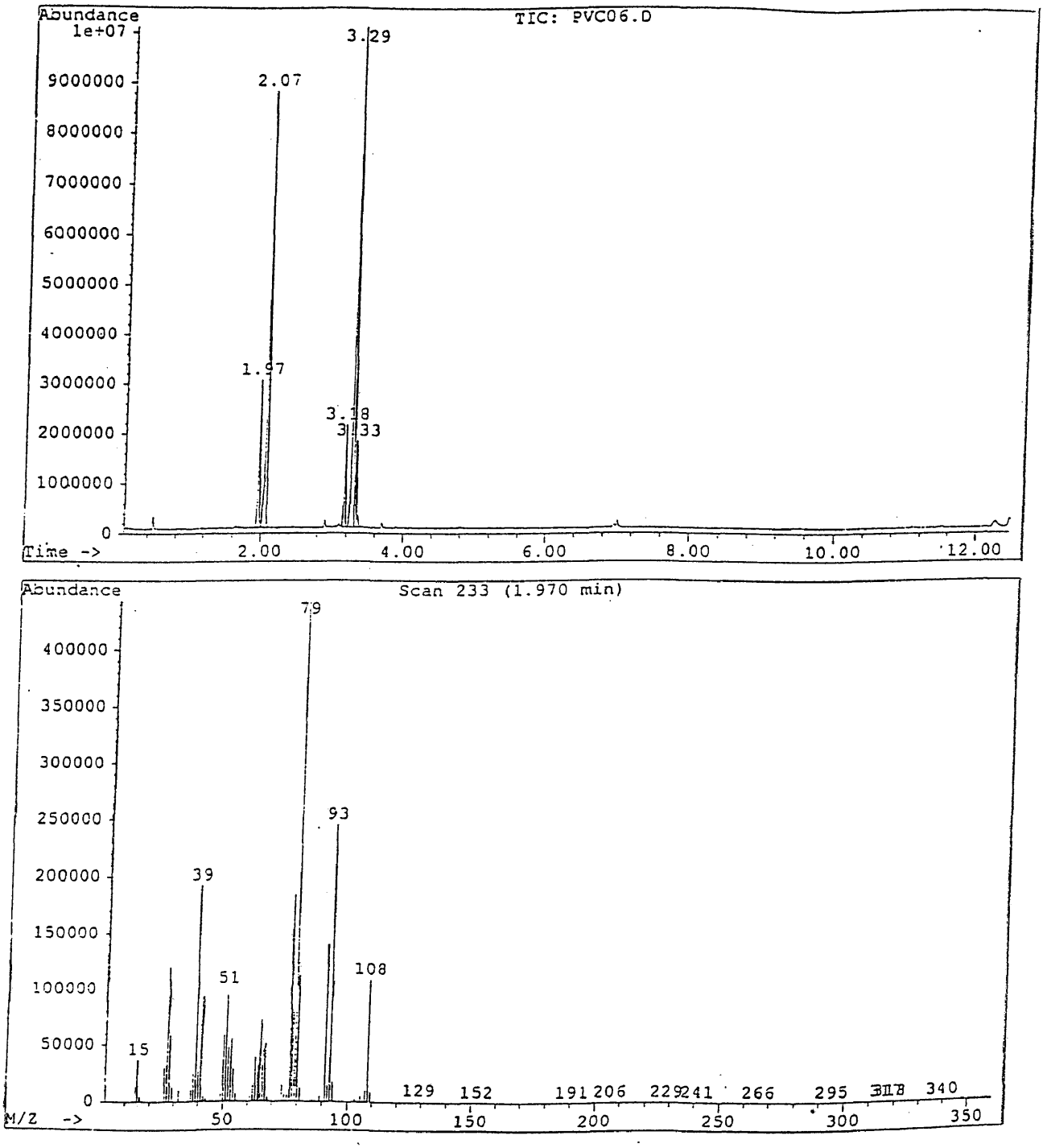


Figure 4-1. GC/MS analysis of products from 2-chloro-1-ethylidenecyclohexane synthesis.

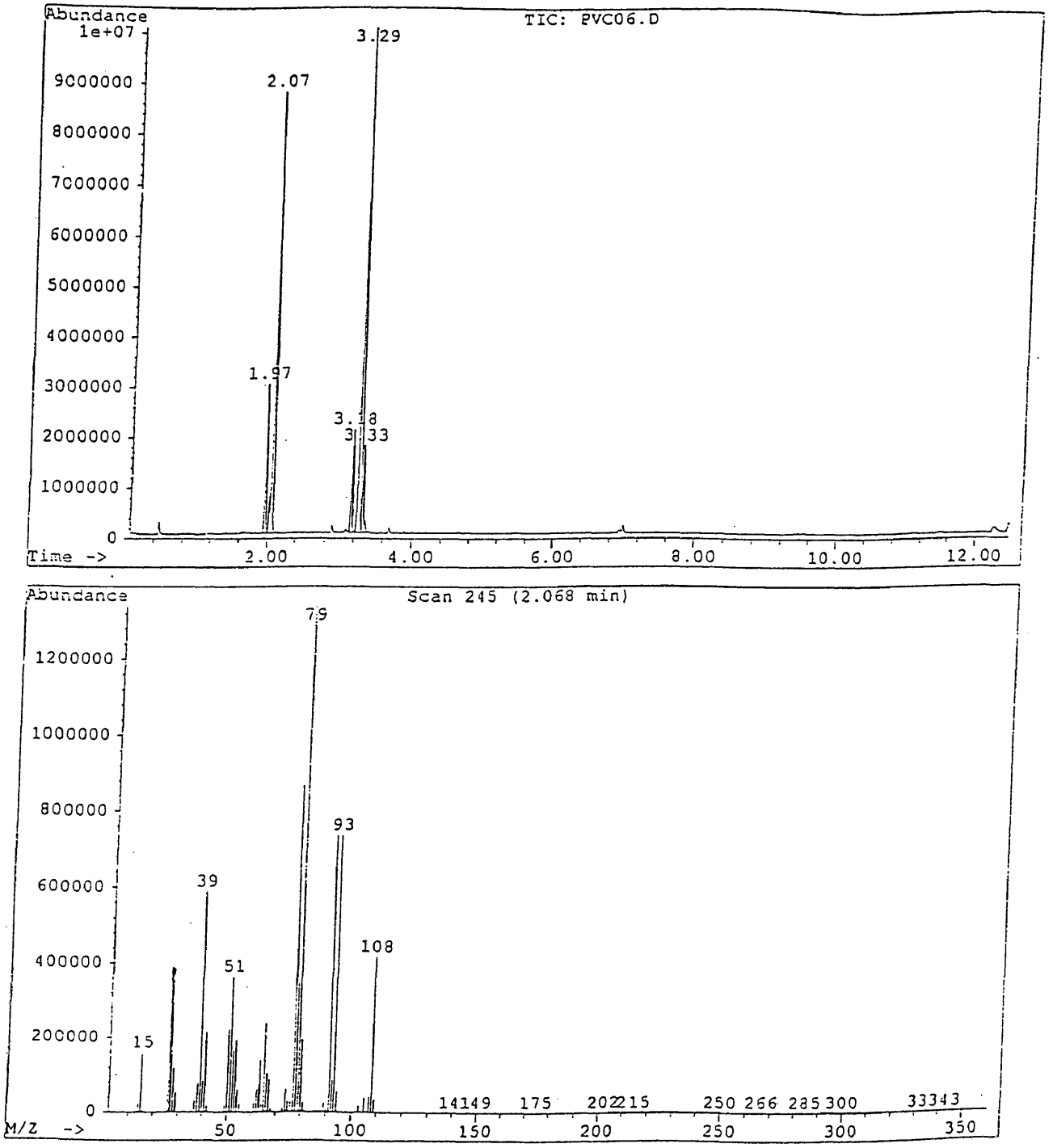


Figure 4-2. GC/MS analysis of products from 2-chloro-1-ethylidenecyclohexane synthesis.

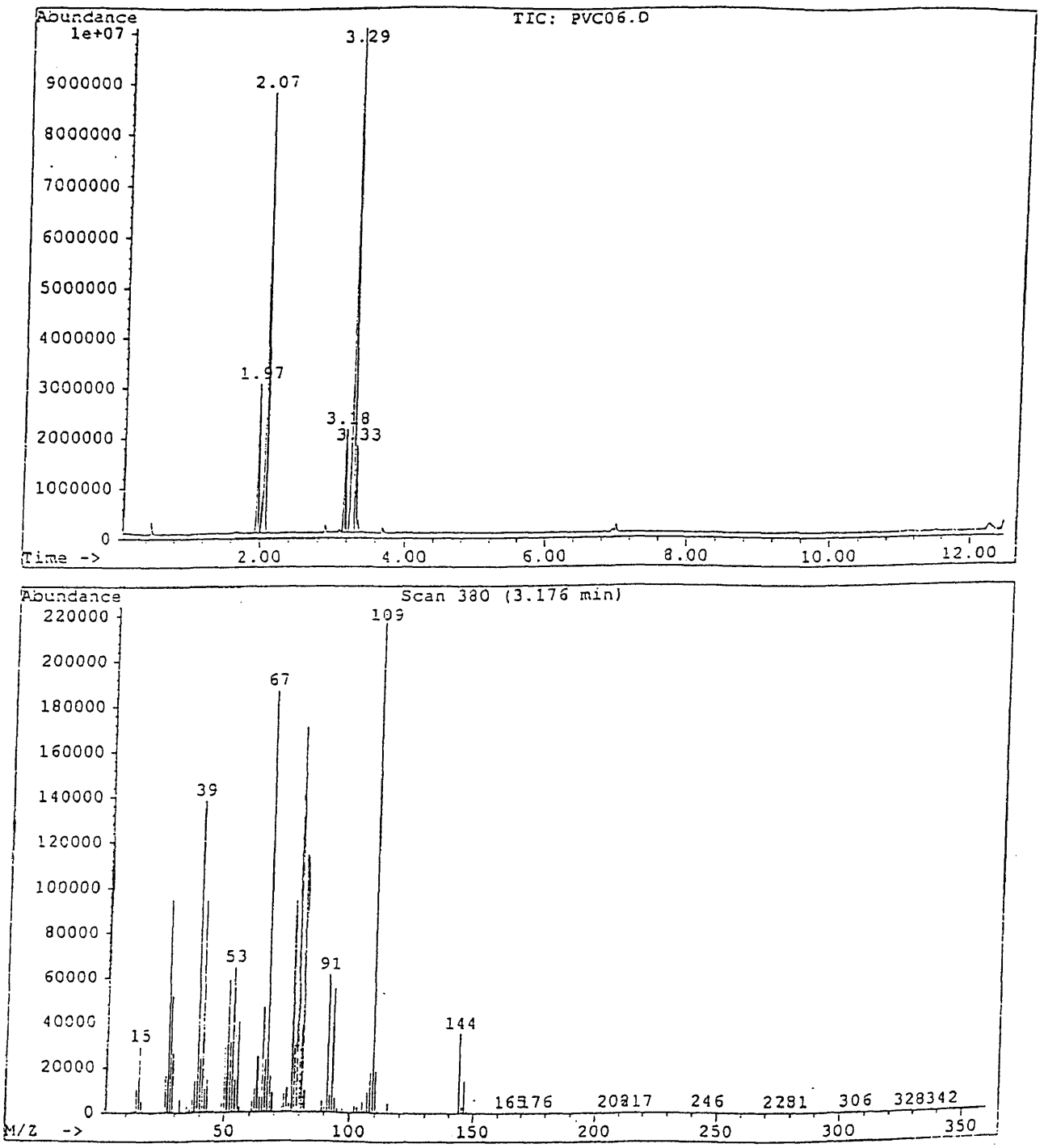


Figure 4-3. GC/MS analysis of products from 2-chloro-1-ethylidenecyclohexane synthesis.

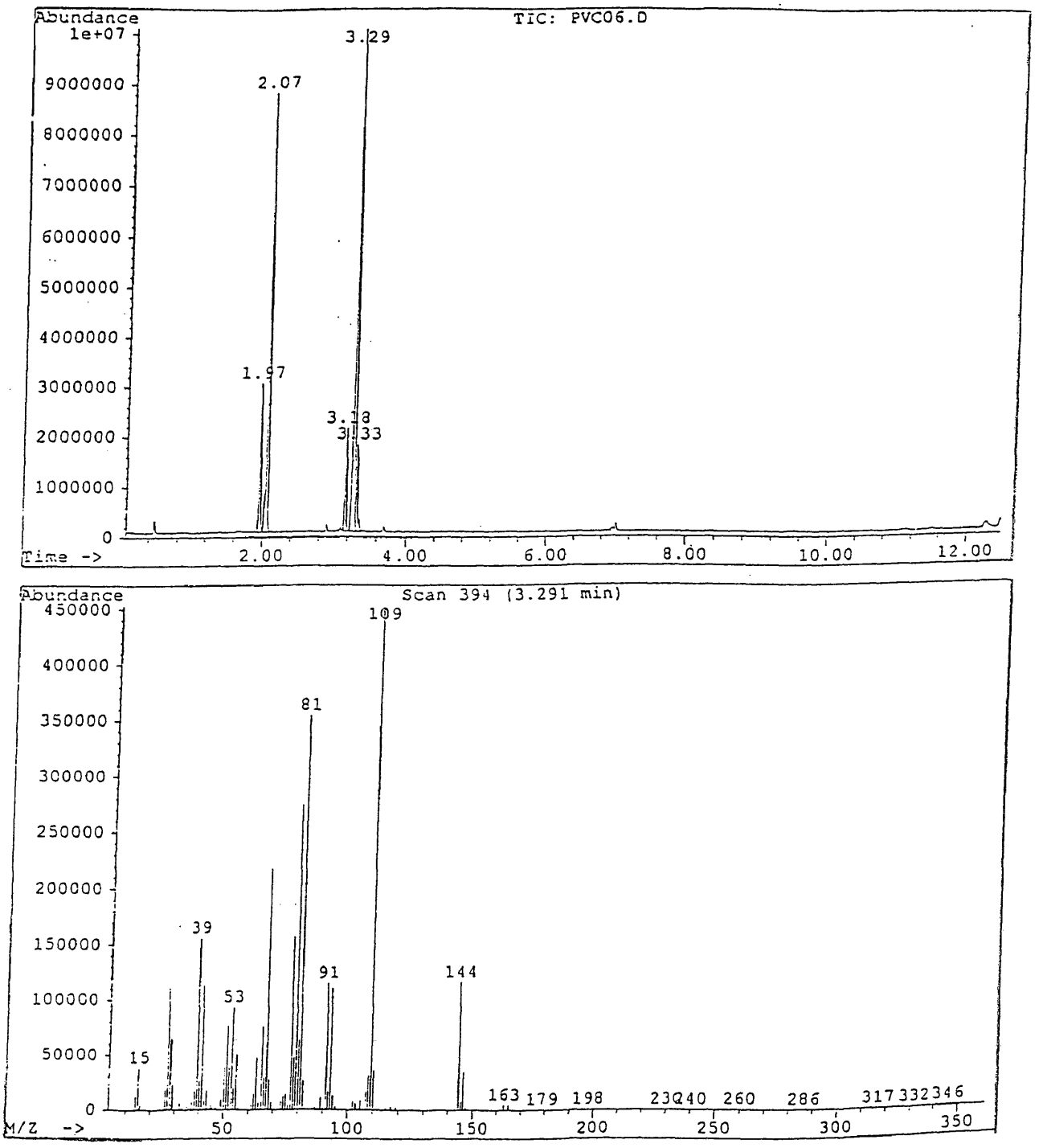


Figure 4-4. GC/MS analysis of products from 2-chloro-1-ethylidenecyclohexane synthesis.

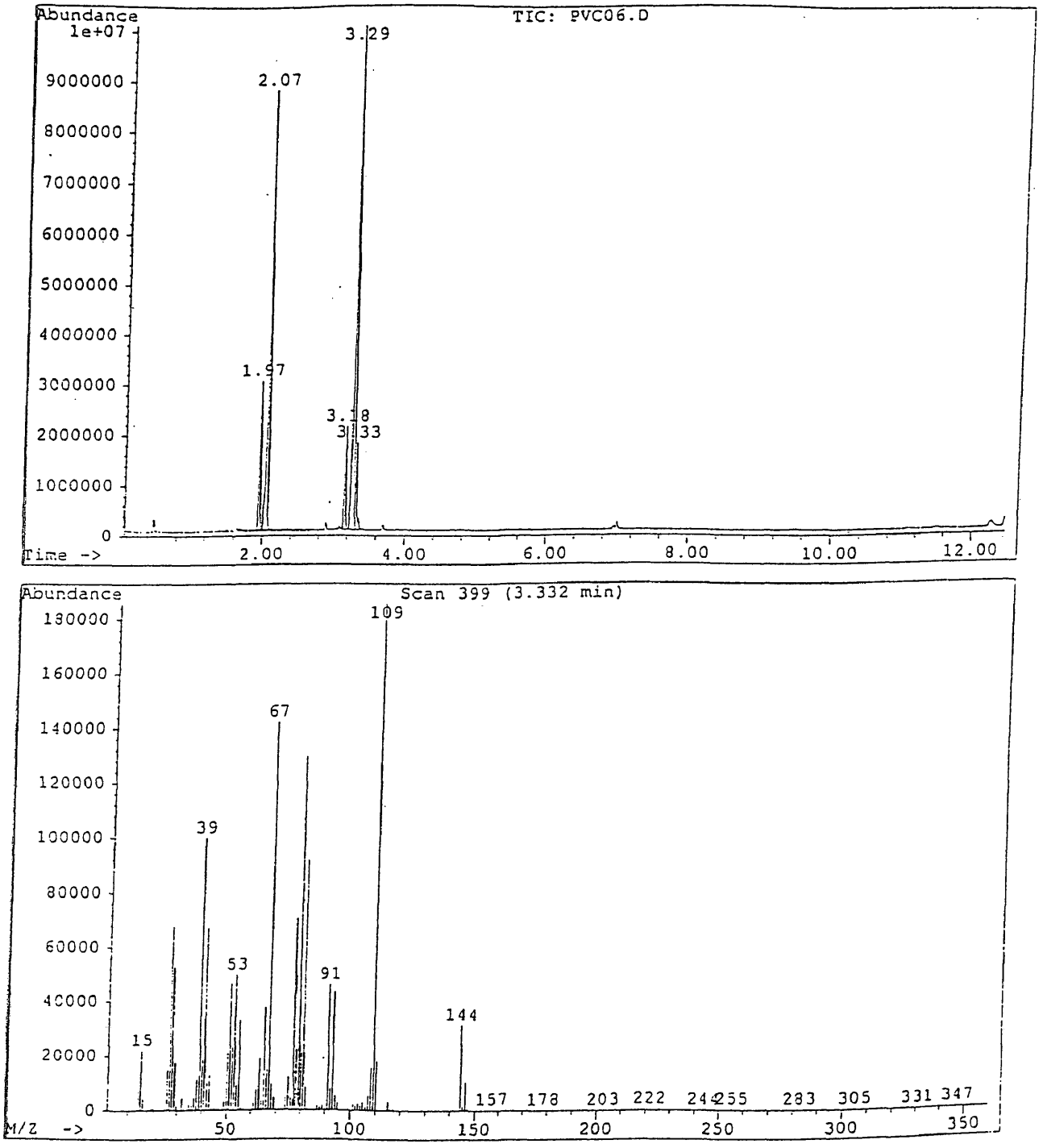


Figure 4-5. GC/MS analysis of products from 2-chloro-1-ethylidenecyclohexane synthesis.

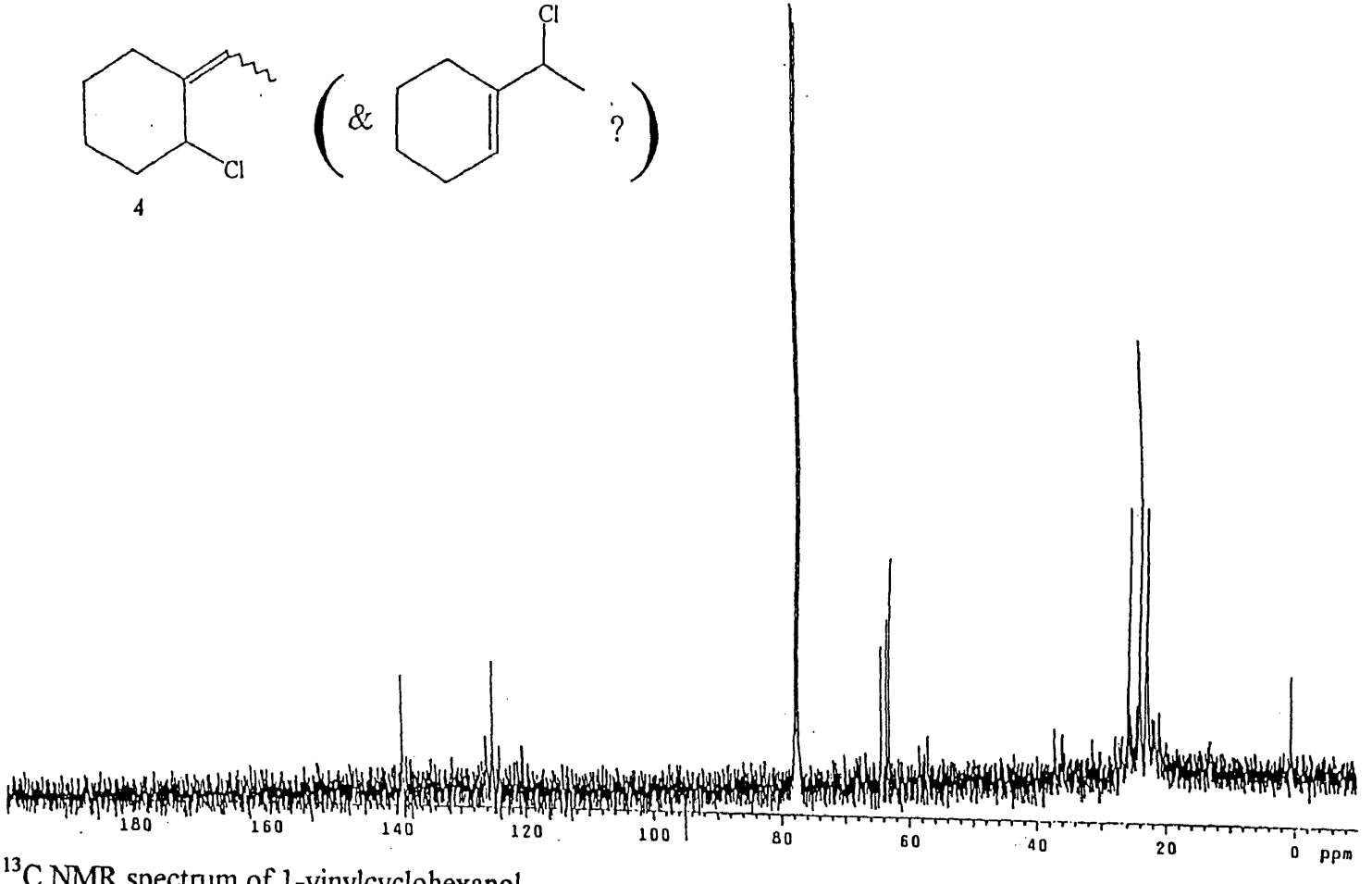


Figure 4-6. ^{13}C NMR spectrum of 1-vinylcyclohexanol.

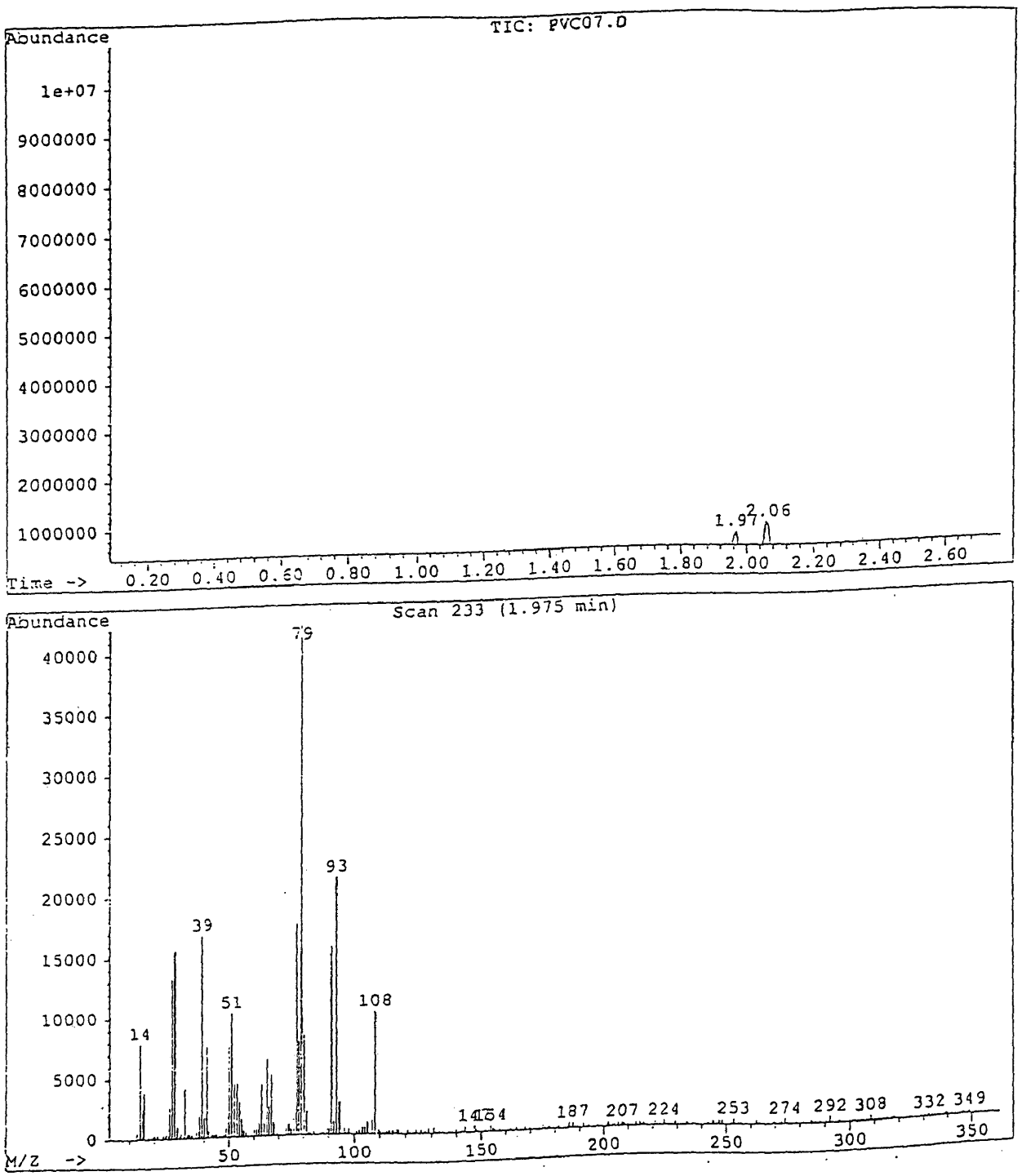


Figure 5-1. GC/MS analysis of diene products from thermal dehydrochlorination.

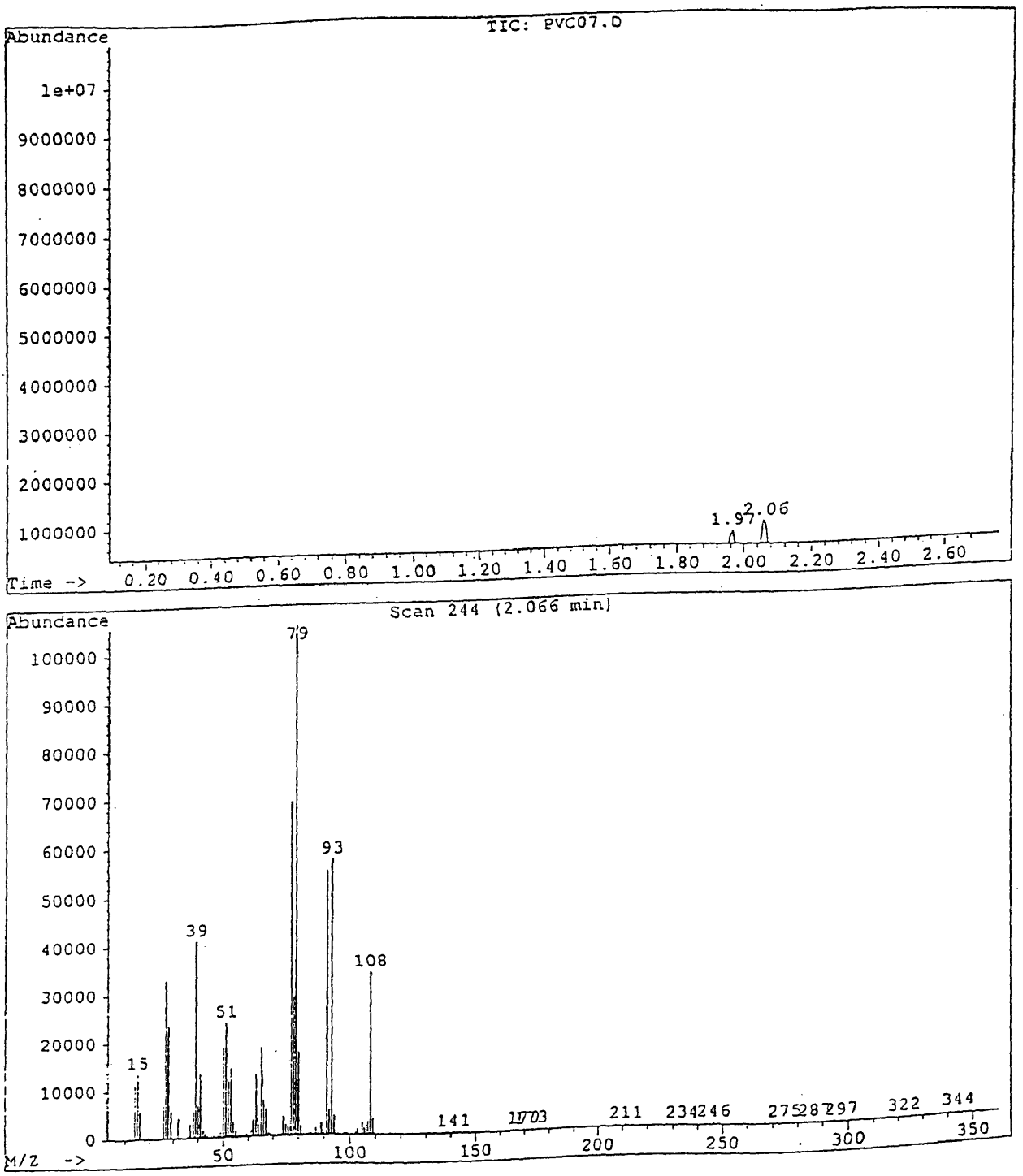


Figure 5-2. GC/MS analysis of diene products from thermal dehydrochlorination.

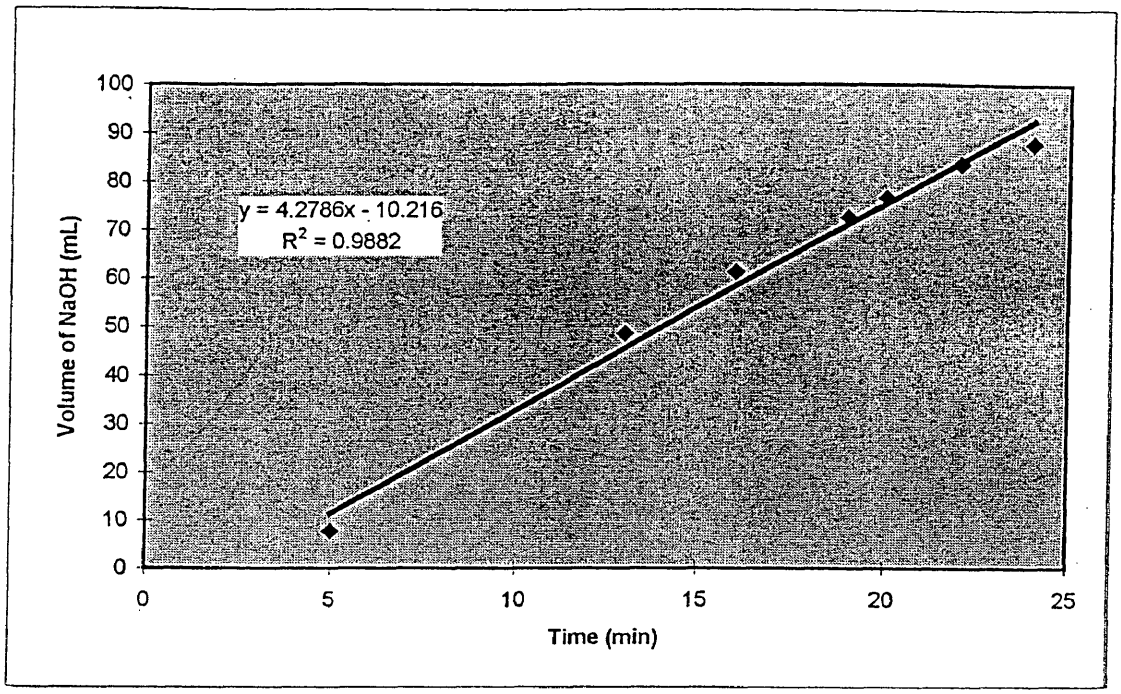


Figure 5-3. Initial-rate kinetic plot for the thermal dehydrochlorination of the allylic chlorides at 170 °C.

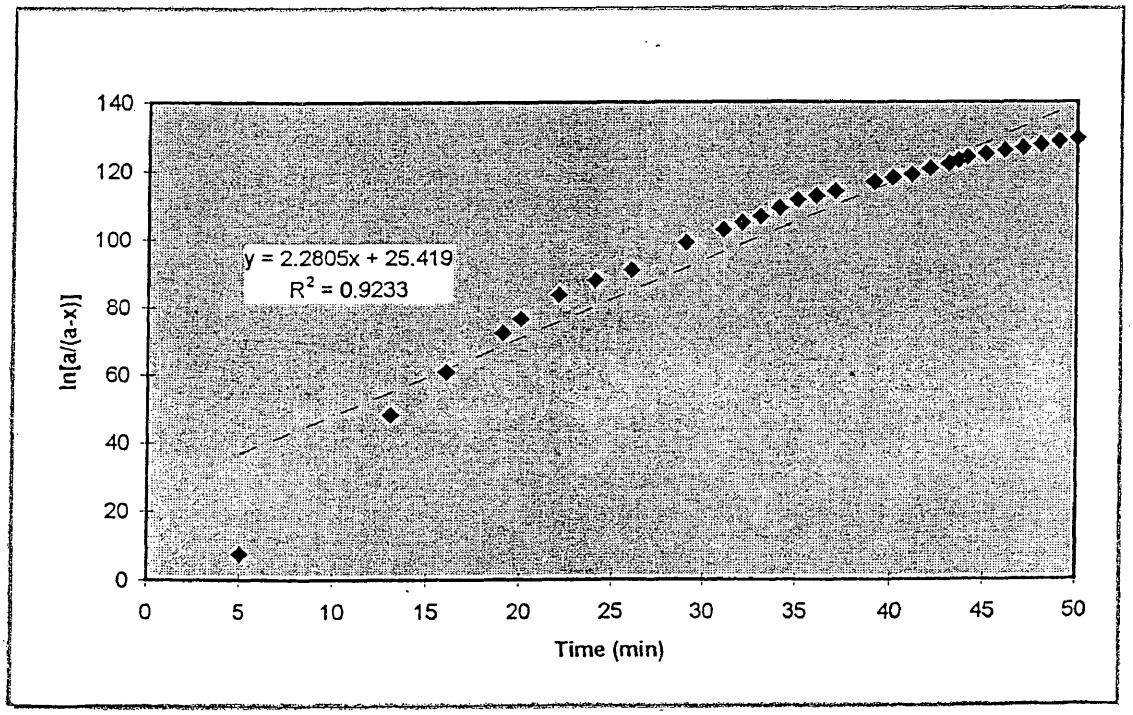


Figure 5-4. Crude first-order kinetic plot for the thermal dehydrochlorination of the allylic chlorides at 170 °C.

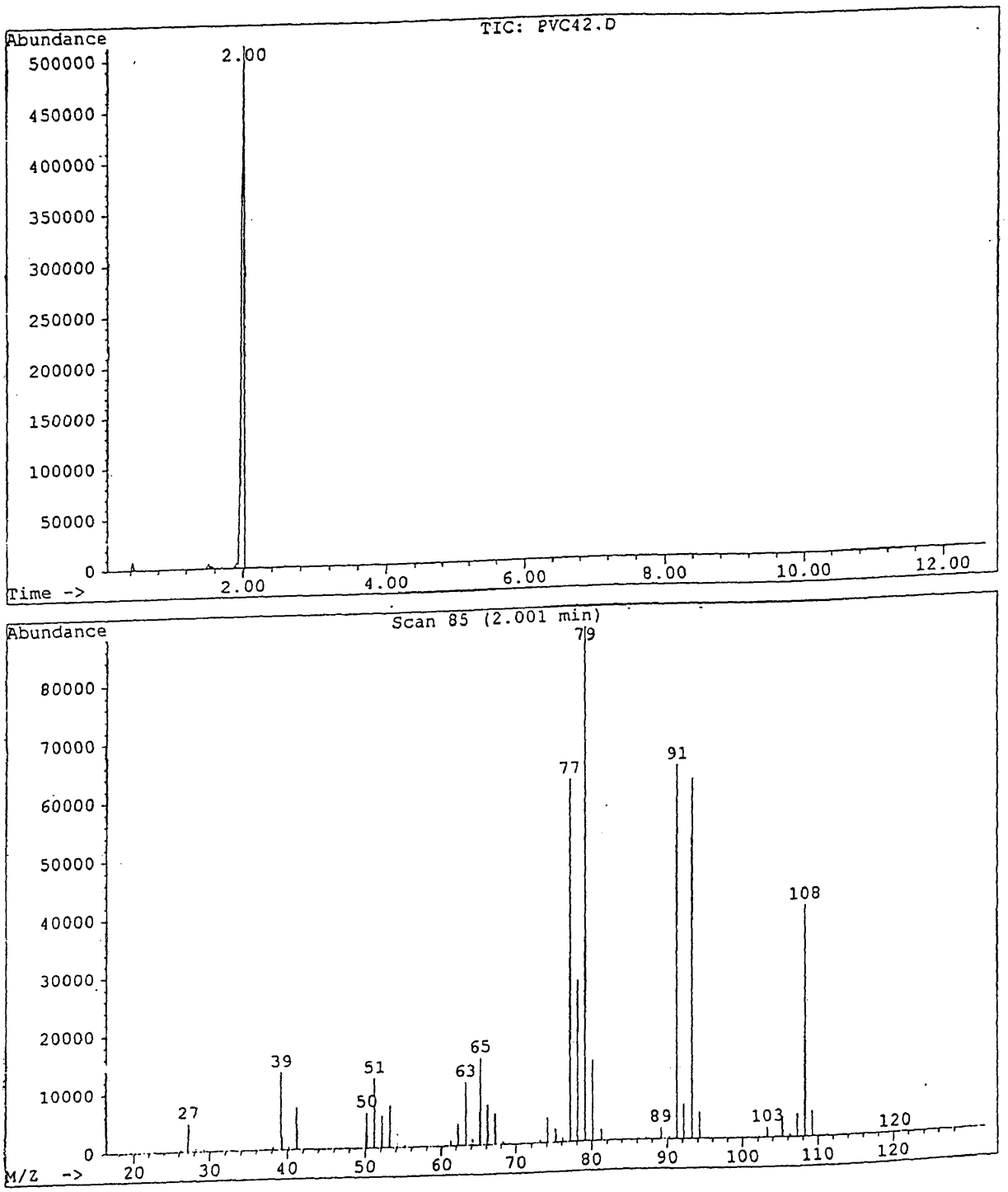


Figure 6-1. GC/MS analysis of the isomerization product of 4-vinylcyclohexene.

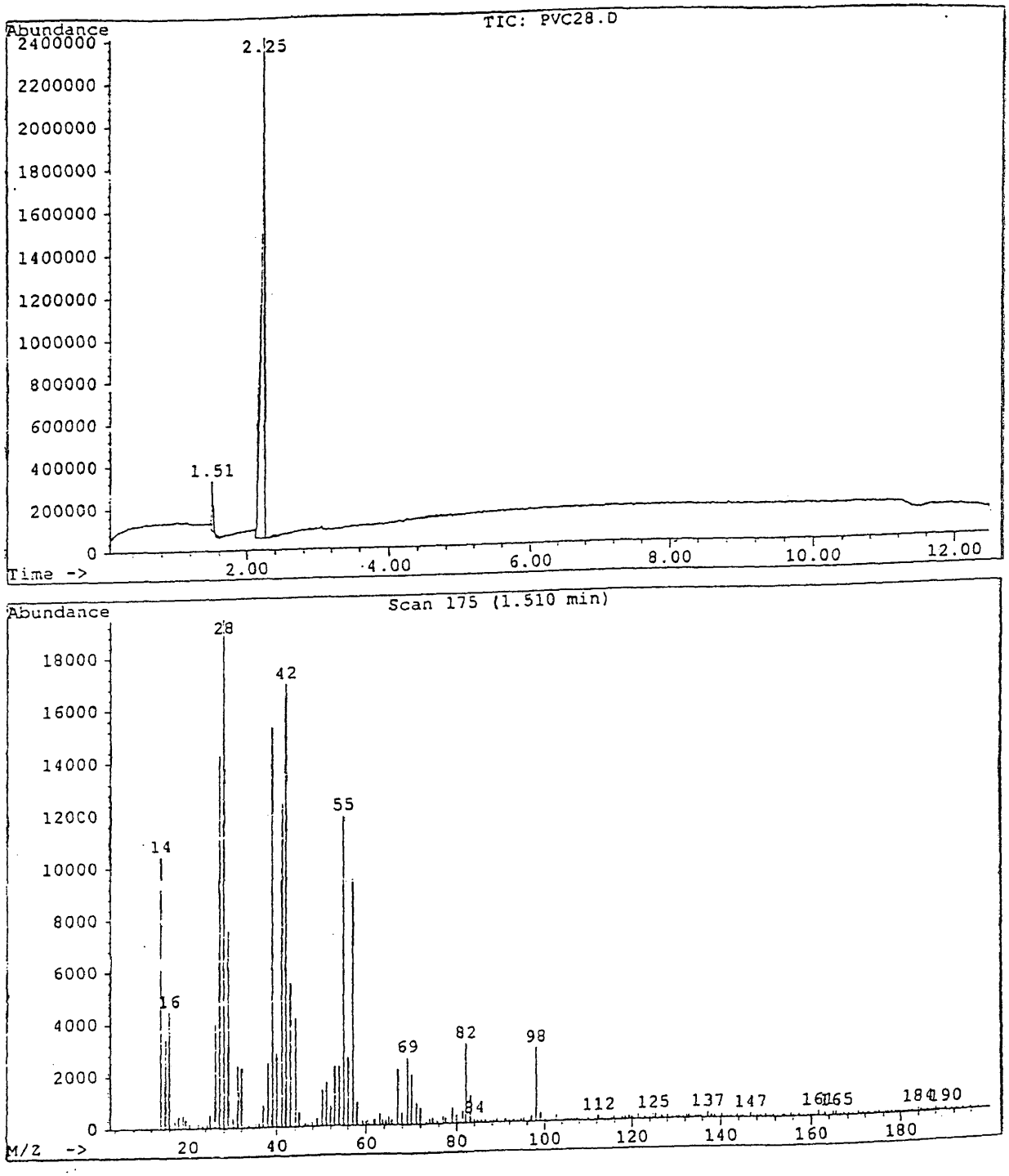


Figure 7-1. GC/MS analysis of the products from the synthesis of 1-vinylcyclohexanol.

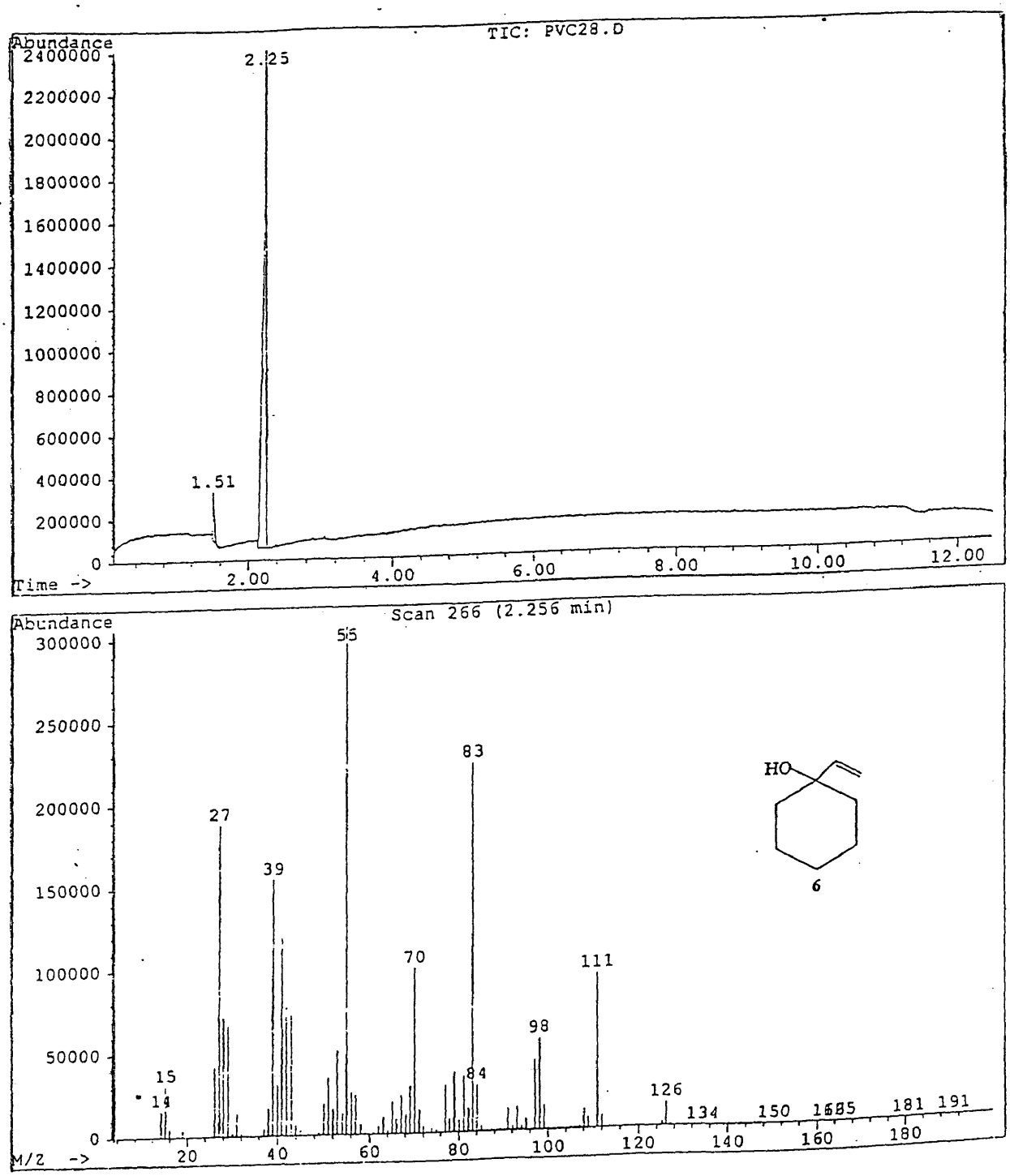


Figure 7-2. GC/MS analysis of the products from the synthesis of 1-vinylcyclohexanol.

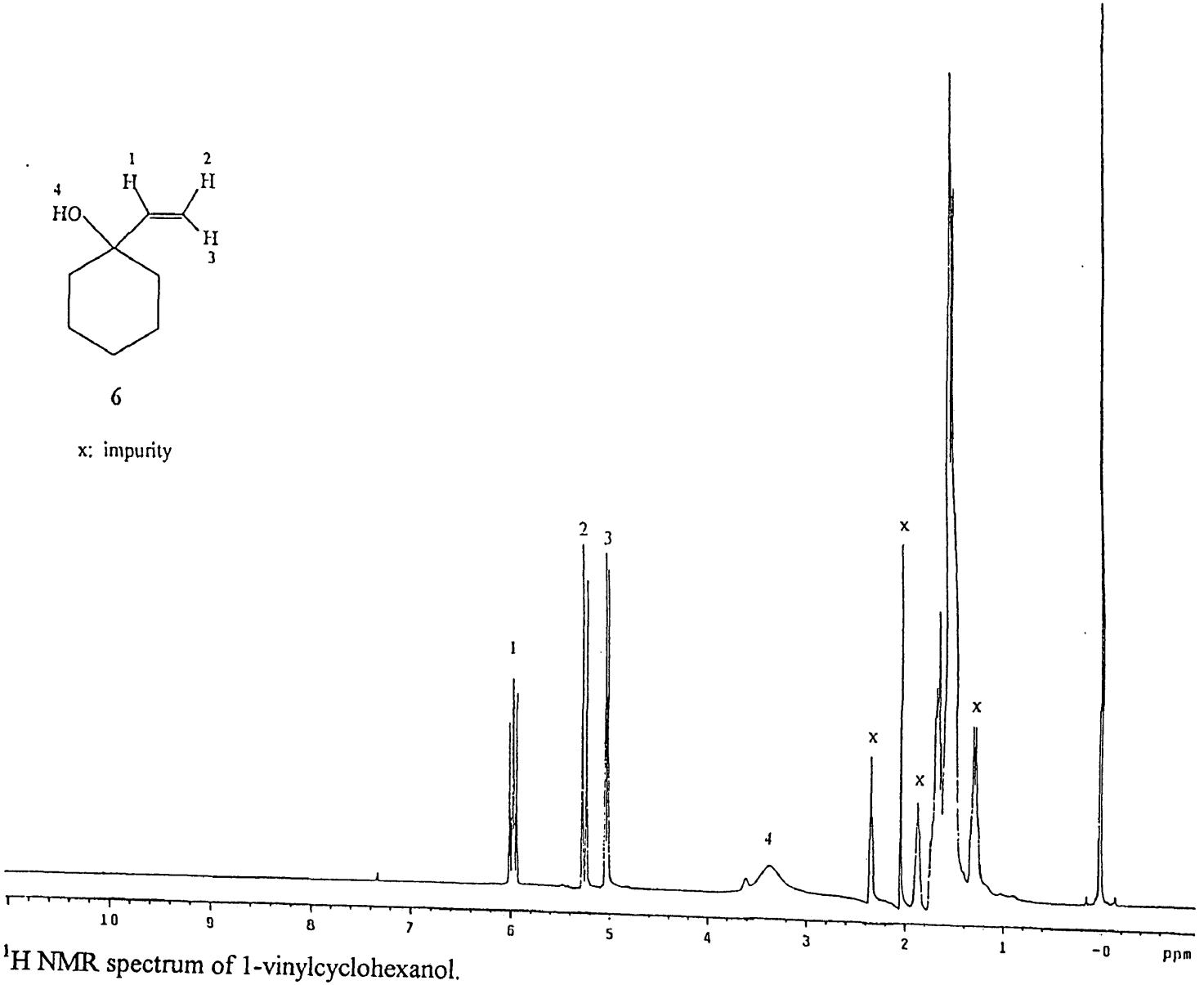


Figure 7-3. ^{1}H NMR spectrum of 1-vinylcyclohexanol.

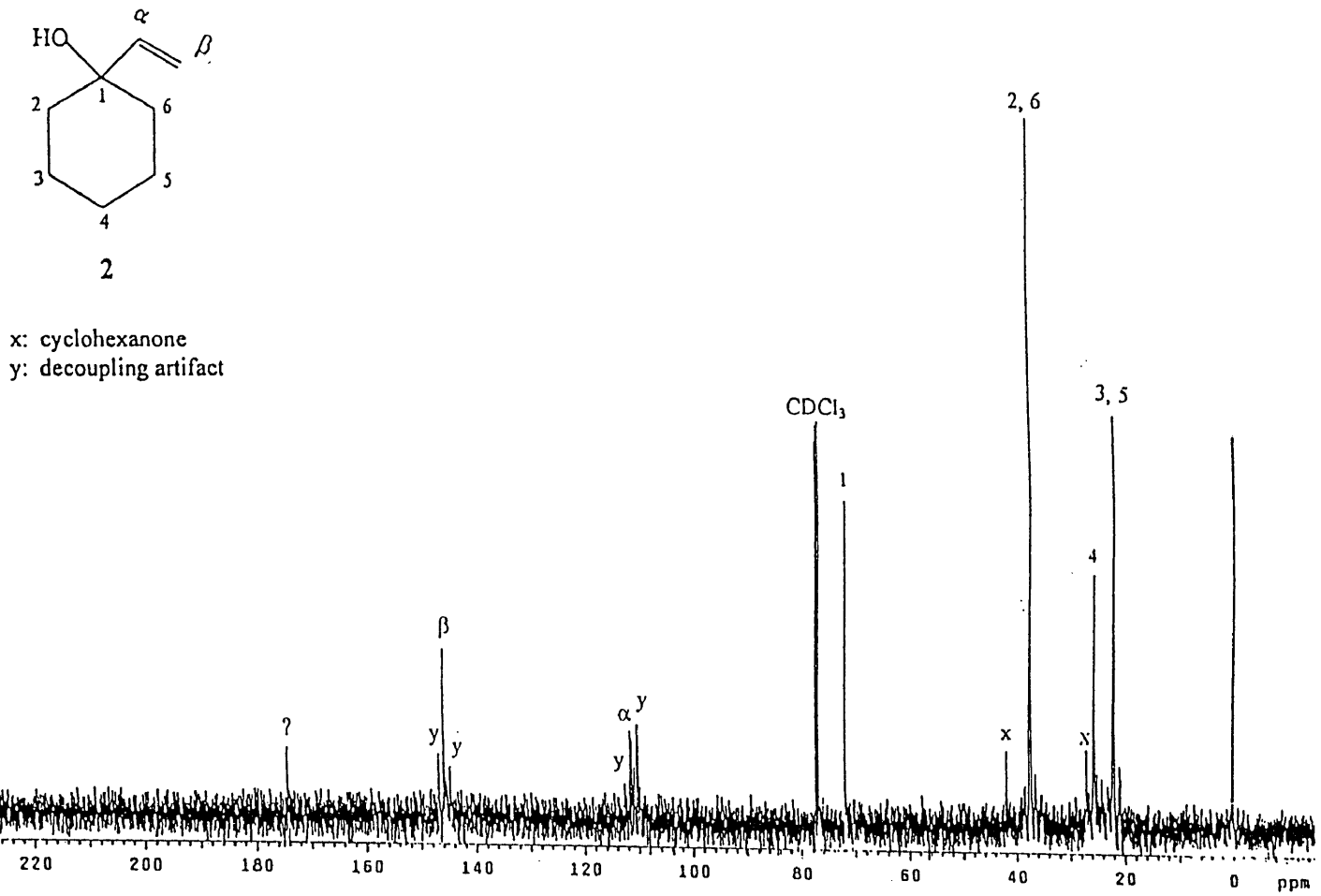


Figure 7-4. ^{13}C NMR spectrum of 1-vinylcyclohexanol.

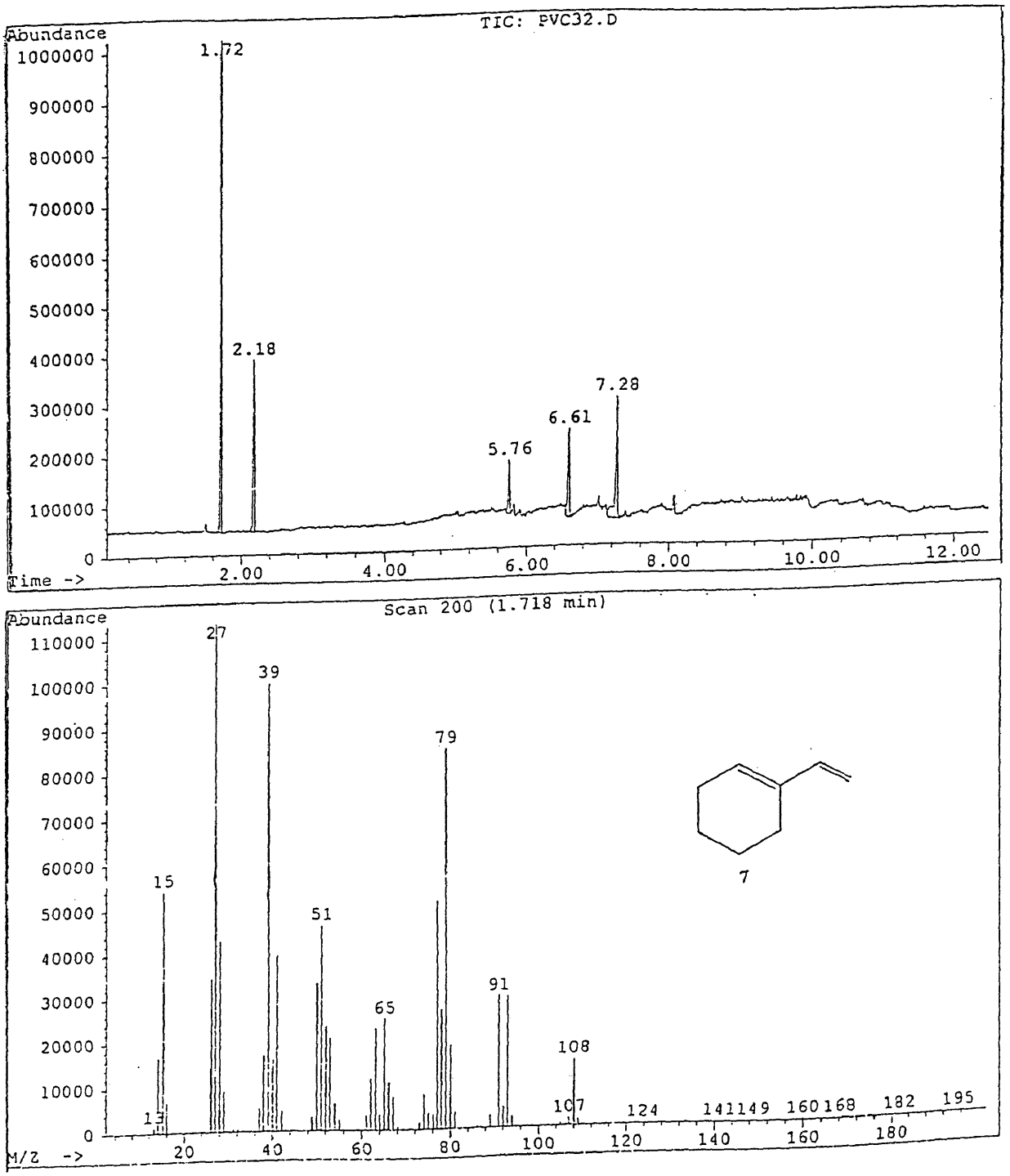


Figure 8-1. GC/MS analysis of dehydration products of 1-vinylcyclohexanol.

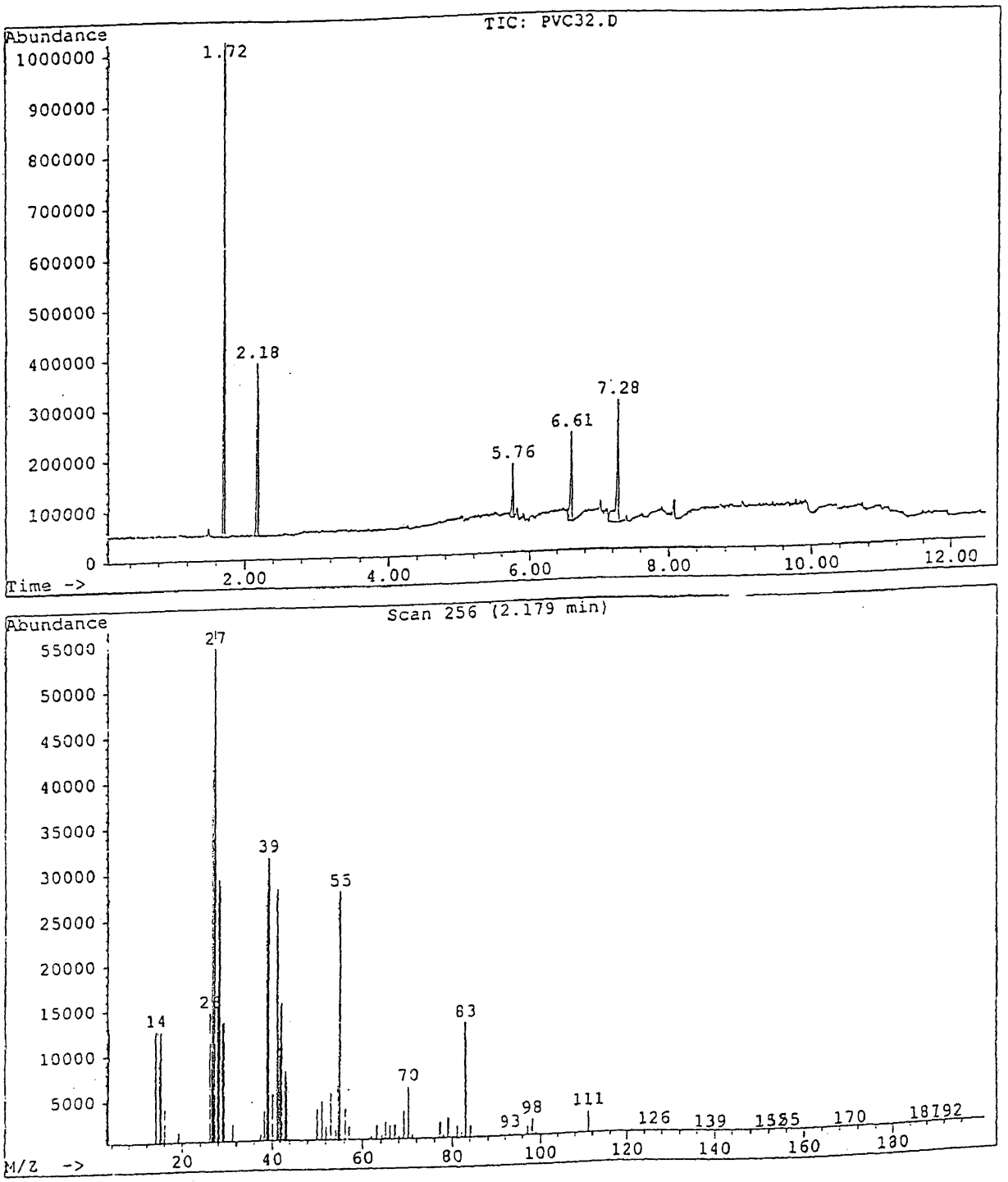


Figure 8-2. GC/MS analysis of dehydration products of 1-vinylcyclohexanol.

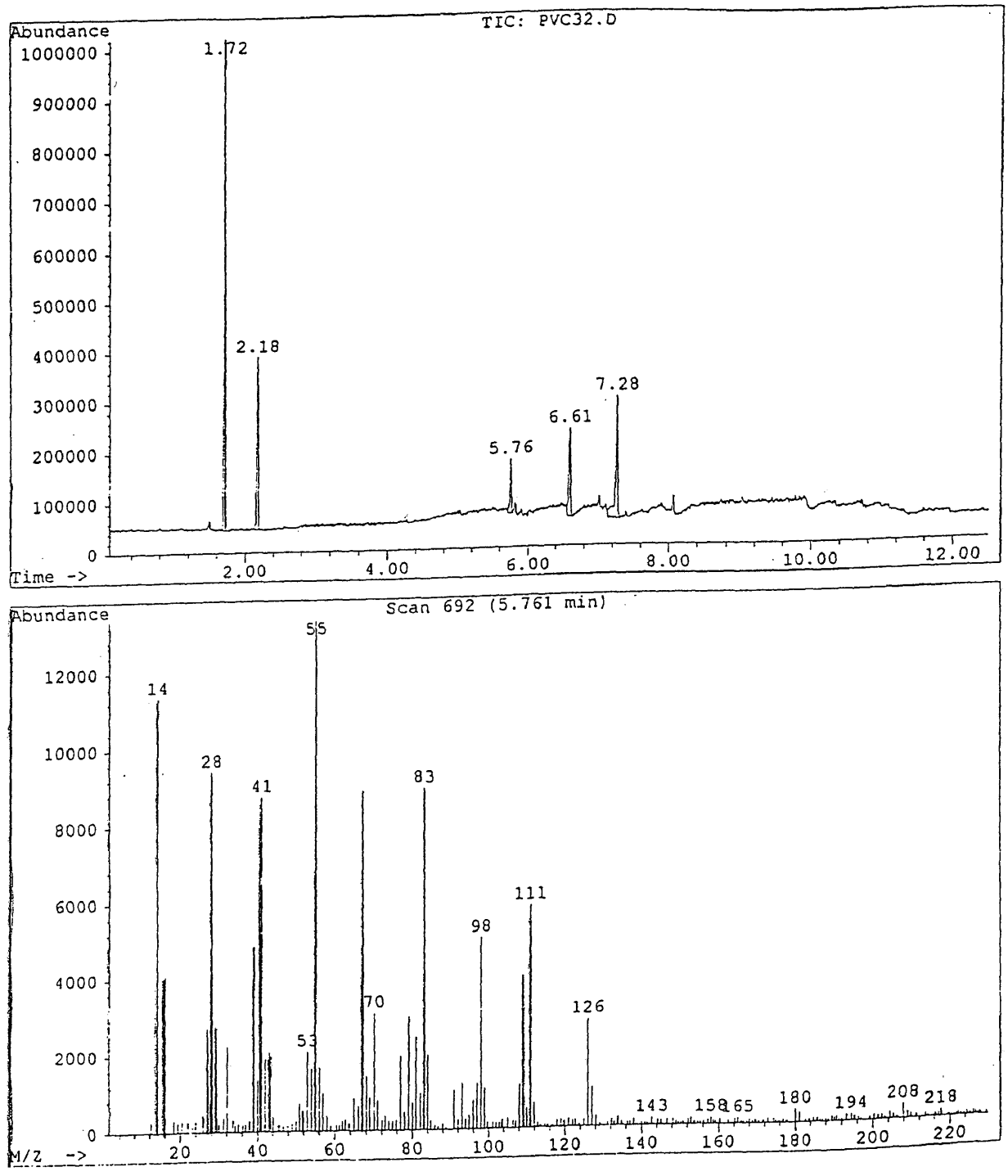


Figure 8-3. GC/MS analysis of dehydration products of 1-vinylcyclohexanol.

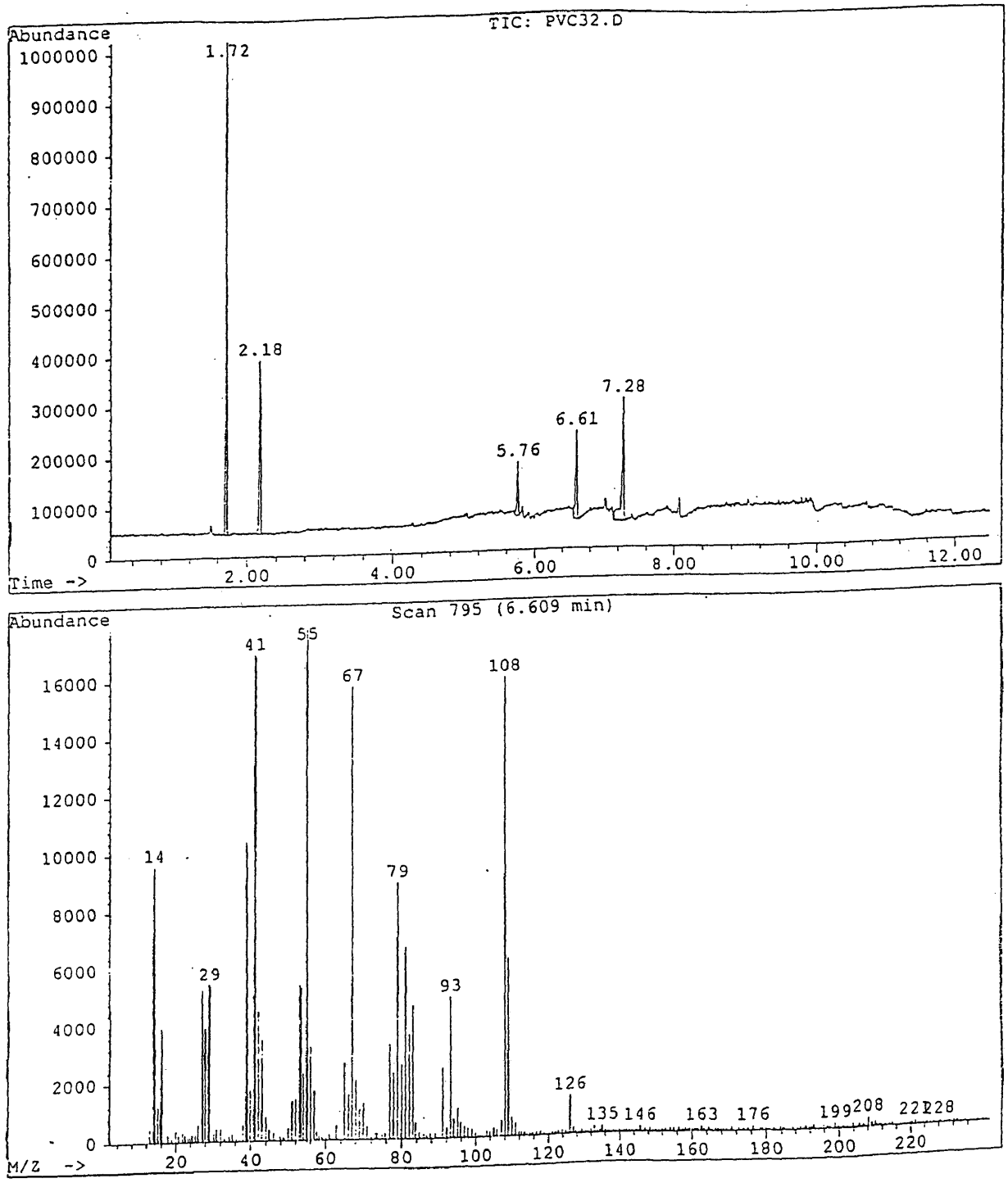


Figure 8-4. GC/MS analysis of dehydration products of 1-vinylcyclohexanol.

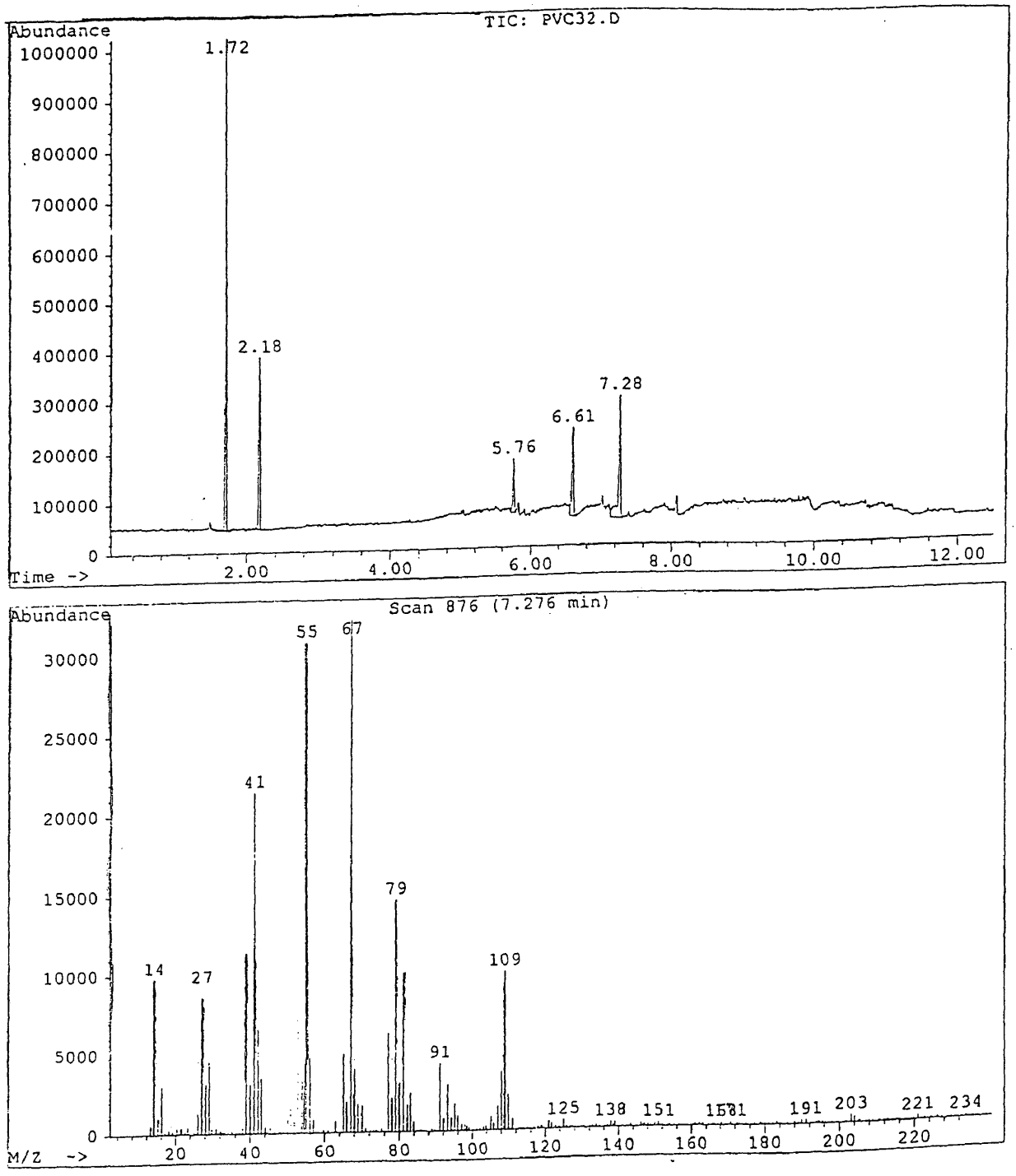


Figure 8-5. GC/MS analysis of dehydration products of 1-vinylcyclohexanol.

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The author was born in Virginia Beach, Virginia on September 15, 1976. She received her high school diploma from First Colonial High School in June 1994. She attended Virginia Tech for her undergraduate education and received the Bachelor of Science degree in Biology in May 1998. She then enrolled in the Master of Arts program in Chemistry at the College of William and Mary in August 1998, and completed this program under the guidance of Dr. William H. Starnes, Jr.